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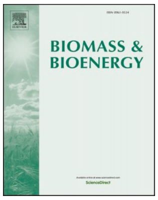

A review of magnetic solid catalyst development for sustainable biodiesel production

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ABSTRACT

Biodiesel is one of the most widely studied biofuels in the literature, which has a bright potential to serve as an alternative source for fossil fuel. Biodiesel is produced from transesterification or esterification reaction and usually requires a catalyst to enhance its product yield. The commercially available homogeneous catalyst generally faces several challenges, including difficulties in product separation, large volume of wastewater effluent discharged from the downstream purification process, and formation of undesirable soap by-product from the reaction between high FFA content feedstock and homogeneous base catalysts. As a result, the application of heterogeneous magnetic catalysts in biodiesel production has attracted many researchers attention due to its relatively simple catalyst separation and higher catalyst recovery rate at a shorter duration. Herein, this review focused on the preparation methods of heterogeneous magnetic acid and base catalysts as well as its effectiveness in biodiesel production. Besides, different synthesis methods of magnetic particles were reviewed as well. The reaction mechanism of heterogeneous catalysts in facilitating the formation of biodiesel via transesterification or esterification processes was also elucidated. For a more sustainable biodiesel industry, more research works are required to utilise waste materials as support for the synthesis of heterogeneous magnetic acid and base catalysts.

1. Introduction

Over the decades, the energy security crisis has been a main issue around the world due to the excessive use of energy by an ever-increasing human population. Moreover, our world economy is highly dependent on the transport of goods, and fossil fuel is the major workhorse of the transportation sector [1]. Due to our high dependency on fossil fuel, energy shortage and environmental degradation have been controversial and the subject of intense debate. These concerns have led to an urgent need for a sustainable bioenergy alternative source. Today, renewable fuels have gained much attention and intensive research works have been underway to develope advanced biofuels from lignocellulosic and oil crop bearing feedstock. Examples of advanced biofuels that widely reported in the literature are biodiesel, bioethanol and biogas. According to the REN21, biodiesel and bioethanol are the most common renewable fuels used in global transportations [2,3]. In particular, the global biodiesel demand has increased by a substantial 15-fold since 2004, and consumption of biodiesel has been growing since then [4]. Generally, biodiesel exhibits high combustion efficiency, low emission level, and excellent lubricity [5]. The adverse effects of global warming, resulting from the increasing consumption of fossil fuel, have became the significant elements that impart a global evolution in developing biodiesel [6]. Biodiesel is one of the most promising renewable fuels that serve a myriad of advantages, including biodegradable, renewable, and environmentally benign. It reduces the emission of carbon dioxide (CO_2), and sulphur significantly [7,8]. Combustion of biodiesel has shown to reduce 78% of the net CO_2 emissions, 46.7% of the carbon monoxide (CO) emission, 66.7% of the

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Abbreviations: Carboxymethyl cellulose, (CMC); Fatty Acid Methyl Ester, (FAME); Free Fatty Acid, (FFA); Hydrochloric acid, (HCl); Megapascal, (MPa); Renewable Energy Policy Network report for 21st Century, (REN21); Sulfuric acid, (H_2SO_4).

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pollution particles such as nitrates, sulfates, organic chemicals, metals and dust or ash particles, and unburned hydrocarbon emissions [9–11]. It can significantly prevent the effect of global warming. Besides, biodiesel can be used in conventional engines by blending it with petroleum-based diesel in a specific ratio by volume (10% biodiesel and 90% petroleum diesel).

Chemically, biodiesel is classified as fatty acid methyl ester (FAME). It is produced from the reaction between fatty acids and methanol under the presence of a catalyst. Meanwhile, the non-catalytic reaction usually consumes more time with lesser yield. Biodiesel can be produced through the most effective method which is the chemical reaction of esterification and transesterification. Transesterification reaction is generally performed by reacting vegetable oil with alcohol under the presence of a catalyst to form fatty acid alkyl ester and glycerol as a by-product. Many types of feedstock have been reported for biodiesel production, including edible oils [12,13], non-edible oils [14,15], micro-algae-based oil [16,17] and spent bleaching clay [18,19].

Traditionally, homogeneous base catalyst is most widely used in the industry over the past decades. It is chemically active and offers a shorter reaction time. Some of the common base catalysts reported in the literature are sodium hydroxide (NaOH) and potassium hydroxide (KOH). KOH is easily soluble in methanol to form sodium or potassium methoxide [20]. By using the homogenous base catalysts, a high methyl esters yield can be obtained under mild reaction conditions at a shorter reaction time. Despite such advantages exhibited from homogeneous base catalysts, the intrinsically high FFA content in natural oil feedstock can stimulate undesirable saponification side reaction, where a large amount of soap by-product are formed and impede the downstream separation and purification processes [21]. As a result, it generates a large volume of wastewater and incurs additional wastewater treatment costs.

On the other side, the applications of homogeneous acid catalysts such as sulphuric acid, hydrochloric acid, and phosphoric acid are suitable for feedstock with a high content of FFA such as waste cooking oil and crude vegetable oil [22]. These catalysts are less sensitive to the presence of high FFA content and water. Homogeneous acid catalysts exhibit high product yield, however the reaction rate is much slower than the homogeneous base catalyst. Alcohol to oil molar ratio is one of the key factors that influence the biodiesel product yield significantly [23]. Despite the high activity of homogeneous acid catalysts, they are highly acidic in nature, which results in severe pipeline corrosion and environmental pollution issues [24]. Besides, the recovery of dissolved homogeneous catalyst within the reaction mixture requires additional washing steps, which makes it difficult to recover and reuse.

The utilisation of heterogeneous catalysts has attained great attention in biodiesel production. It is neither consumed nor dissolved during the reaction, which makes it easy to separate and recycle. It also exhibits a better catalytic performance in comparison to the homogeneous catalyst. In a study by Veljkovic et al., CaO catalyst was used as heterogeneous catalyst in the production of biodiesel from Sunflower oil and achieved 98% of biodiesel yield using 1 wt% catalyst loading [25]. In another study by Muthu et al., a sulfated zirconia was used for biodiesel production and obtained 95% of yield from Neem oil [26]. Hence, it shows that using heterogeneous catalysts can minimize the process of biodiesel production and able to catalyse high acid value oils. Moreover, it is non-corrosive and easy to separate/recycle without the need for any regeneration treatment [27]. Several types of heterogeneous catalysts are available for a base-catalysed reaction such as metal oxide, mixed oxide, and transition metal oxide, ion exchange resin, carbon-based catalysts, and zeolite [28]. Nevertheless, these solid catalysts produced from non-renewable materials generally displayed several downfalls, such as high production cost, high toxicity, highly susceptible to leaching, high microporosity with little acid sites on the surface, and non-environmentally friendly [29,30]. Conversion of lignocellulosic biomass waste into solid catalysts has been investigated and studied extensively in recent days. Development of biomass-derived catalysts could reduce the catalyst synthesis cost and also offers an ideal solution for the biomass disposal issue. In the literature, biomass resources are used extensively as a sustainable feedstock for biofuel production via several methods such as heating, fermentation and conversion to gas or liquid fuel [31]. Synthesis of heterogeneous biomass-derived catalysts could also serve as a sustainable solution to be assimilated into biofuel production process since the application of such catalyst is non-toxic, recyclable, and easy to separate [32].

Although different types of solid acid catalysts have been proposed to serve as a potential catalyst for esterification reaction, however the presence of sulphur impurities in the feedstock could impede the catalytic activity of such catalysts [33]. According to He et al. [34], waste cooking oil and animal fats may content high sulfur due to the presence of sulfur containing compounds such as proteins. Meanwhile, the leaching from the surface of the solid catalyst is possible due to the presence of water during the reaction which might contaminate the biodiesel and decrease the usability of solid catalyst [35]. Therefore, novel solid acid catalysts with high catalytic performance and excellent deactivation resistance are highly sought for industrial biofuel production. As an effort to address such gap, the use of magnetic materials as the catalyst support for the transesterification reaction has been attempted by several researchers and such applications have attracted much attention in the literature since then. Magnetic particles are a form of nanoparticle which can be separated by using external magnetic fields. Metallic magnetic particles usually consist of cobalt and nickel, alloys: iron or platinum, metal oxides: iron oxide, and ferrites [36]. Besides, magnetic nanoparticles can be well-dispersed within the reaction mixtures. It also provides a larger surface area and improves the accessibility of reactants into the active sites. Instead of applying the conventional time-consuming filtration and centrifugation steps, the removal of magnetic nanoparticles catalysts from the product mixture can be easily assisted by a simple magnetic field separation in post reaction treatment [37]. Moreover, it can be recycled multiple times with minimum loss in catalytic activity. Magnetic catalysts are well known as a “bridge material" that links both homogeneous and heterogeneous catalysts. It shares the properties of both homogeneous catalysts (high activity) and heterogeneous catalysts (easy separation) in one single catalyst.

As a whole, this review focuses on the synthesis of magnetic solid acid and base catalysts for biodiesel production. The preparation method and catalytic performance of magnetic heterogeneous catalysts in biodiesel production are discussed critically. This review aims to provide an insightful idea on the recent development, new preparation method, and catalytic performance of solid magnetic catalysts for the production of biodiesel.

2. Feedstock for biodiesel production

The primary energy supply in the world comes from fossil fuel and one of the feasible alternative sources in replacing fossil fuel is biodiesel. In 1984, biodiesel production was initiated where, scientists conducted experiments to product biodiesel from vegetable oil and the first biodiesel manufacturing plant was started in Austria [38]. Later, the development of biodiesel in the United States was developed by the National Soy Diesel Production Board in 1992 [39]. Since then, synthesis of biodiesel has been well received as one of the first alternative diesel fuels chemically similar to fossil fuel. It consists of several superior characteristics: (a) excellent resource renewability, which maintains continuous supply throughout the year, (b) biodegradability with minimum emission of noxious compounds, (c) reduces heavy dependency on the crude oil imports, (d) eco-friendly with lower emissions of sulphates, aromatic hydrocarbons, CO_2, CO and particulate, and (e) rich in oxygenates which promotes complete combustion and lower greenhouse gases emission [40]. Biodiesel has been incorporated as a blended fuel component in the transport sector as it exhibits similar chemical properties with petroleum diesel and proved to emit lower greenhouse gases.

The pollutants emitted from the combustion of fossil fuels have a significant effect on the atmosphere and human health. As stated by the United Nations Intergovernmental Panel, global warming is mainly caused greenhouse gases emission such as methane (CH_3), nitrogen oxides (NO_2), and CO_2 [41]. Hence, the use of biodiesel could be a potential solution in reducing the concentration of pollutants and carcinogenic elements released into the atmosphere.

Currently, more than 350 oil-bearing crops are recognized worldwide as potential sources for biodiesel production [42]. The variability of crop feedstock is an essential factor in determining the profitability of biodiesel production. A good biodiesel feedstock should have a low production cost and high biodiesel yield. Generally, the raw feedstock cost accounted about 75% of biodiesel production costs [43,44]. Therefore, biomass feedstock selection is a key consideration for biodiesel production as it may affect many other factors, such as cost, yield, composition, and purity. The selection of biodiesel feedstock typically varies considerably with regional availability. For instance, palm oil is one of most important biodiesel feedstocks in Malaysia and other tropical countries due to its abundance availability. Meanwhile, soybean oil and rapeseed oil are two essential feedstock resources of biodiesel production in the United States and European countries [45–47]. Table 1 shows the biodiesel production and percentage of global production in the year of 2015. The suitability of feedstock in biodiesel production was investigated and categorized as edible oils, non-edible and algal oils. The advantages and disadvantages of each oil crop bearing feedstock for the production of biodiesel were discussed in detail.

2.1. Edible oils

Biodiesel production using vegetable oil feedstock was started in the year of 1980. The conversion of edible oil to biodiesel was the most preferred option back then since it is chemically feasible [49]. Edible oil is known as first-generation feedstock for biodiesel production. Up today, approximately 95% of the biodiesel production in the world was produced from edible oils. Some of the commonly used edible oils are sunflower oil, rapeseed oil, soybean oil, corn oil, and palm oil [50]. It is reported that approximately 80% of total biofuels production in the European Union was made from rapeseed and sunflower seed oils. Table 2 shows the production and oil yield percentage of first-generation biodiesel feedstock. The low acid value in the first-generation feedstock is suitable for the use of homogeneous base catalyst. Based on the current biodiesel scenario, the use of different edible oils in the production of biodiesel had a significant global impact on the food industry [51,52]. From the global annual report, there are nearly 4 billion tons of petroleum consumption and 0.1 billion tons of vegetable oil production. As a result, the world may face crucial 'food versus fuel' issue in the future [53]. The rising demand of these oils for biodiesel production has caused a steep surge in both biodiesel and edible oil production costs. Moreover, such growing demand also affected the environment as it requires more land hectares to cultivable, such as oil bearing crops, contributing to major deforestation in tropical countries [54]. Continuation of such issue will impact the alarming climate change, which eventually affects the environment and human health adversely.

Table 1
Biodiesel production by region and percentage of production in 2015 (REN21, 2016 [48]).

Country	Biodiesel production (billion litres)	Percentage of world production (%)
European Union	13.5	43
United States	4.8	15
Brazil	4.0	13
Argentina	2.1	7
Indonesia	1.2	4
Thailand	1.2	4
Malaysia	0.6	2
Colombia	0.6	2
Canada	0.3	1

Table 2
Production of edible oils for biodiesel production (Oil World Annual 2013 [55]).

Feedstock	Production, million tonnes	Oil content, %
Soybean oil	41.8	18–20
Palm oil	52.8	30–60
Hemp seed oil	5.93	22–38
Rapeseed oil	24.2	38–46
Sunflower oil	14.9	25–35
Corn oil	2.68	24–44
Coconut oil	3.24	63–65
Peanut oil	3.85	45–55
Olive oil	3.35	45–70

2.2. Non-edible oils

With the high production cost of edible oils and its adverse influence on the global food market, the researchers turned their interests in using non-edible oil as an alternative feedstock [56]. Non-edible oil is generally unsuitable for human consumption. It can be grown on barren lands. Example of non-edible oils include plant oils, waste oils, and animal fats. They are also called second-generation oils [57]. Apart from the inherent low production cost and low toxicity, there are many reasons to use non-edible oils for biodiesel production. First, many oil plant crops are rich in non-edible oils, which can easily be grown in low-cost land. Low-cost lands or marginal lands are often lack of water, low soil fertility and high temperature. There are some biofuel crops that can sustain the environmental condition where food crop may not be able to cultivate such as cassava, *Jatropha* and Pongamia are the essential tree crops that can sustain dry conditions [58]. By growing these plants, the atmospheric concentration of carbon dioxide can be reduced [18].

More than 26 plant species were reported to be potential sources for non-edible oils production as biodiesel feedstocks [59]. Table 3 illustrates the types of feedstock and the percentage of oil yield for second-generation biodiesel feedstock. To date, non-edible oils from *Jatropha*, Pongamia, and rubber seeds are widely reported in the literature for biodiesel production due to their high availability and low production costs [60]. The benefits of producing fuel from non-edible oil

Table 3
Production of non-edible oils for biodiesel production [4,55,66,67].

Feedstock	Oil content, %	FFAs content, %
Jatropha oil	20–60	9–28
Pongamia (Karanja) oil	30–40	8–20
Rubber seed oil	40–50	7–11
Cottonseed oil	18–25	0.4–11
Neem oil	25–45	9–30
Melia azedarach (syringa oil)	10–45	
Moringa oleifera	30–40	1.3–2.9
Calophyllum inophyllum	60–75	22–54
Nicotiana tabacum	33–40	17–35
Madhuca Indica (*mahua* oil)	30–45	19–20
Sapindus mukorossi (soapnut oil)	23–51	
Jojoba oil	45–55	20–28
Chinese tallow seed oil	24–32	19–40
Waste cooking oil		0.42–37
Waste coffee oil	10–15	2.1–4.6
Waste fish oil	1.4–40	4.9–28
Beef tallow		0.29–10
Chicken fat		11–13
Brown grease		15–40
Waste fryer grease		2.7–5.6
Tung oil	16–18	9.5–11.1
Tall oil		~100
Acid oil		~59.3

are lower particulate matter, CO, NOx, hydrocarbons and smoke emissions [61]. Besides, animal fats are also often used as biodiesel feedstock. However, the poor availability of animal fats could not satisfy global fuel demand [62]. On the other hand, animal fats tend to solidify under room temperature, which could cause additional operating difficulties during the production process. Waste cooking oils are two to three times less expensive than vegetable oils, however the availability of waste cooking oils depends on the use of edible oils [63,64]. Moreover, waste oils may have high moisture content, particulate matters and FFA due to the exposure to high temperature and food processing. Accordingly, the waste oils need to be pre-treated prior to esterification reaction [65]. Despite all above, the drawback of using non-edible oils in biodiesel production is the intrinsically high FFA content, which requires an additional pre-treatment process to reduce the FFA content before transesterification reaction. In general, the availability of edible and non-edible oils is rather limited and could not satisfy the worldwide biodiesel demand.

2.3. Microalgae biomass

Recently, many research works have been attempted to produce biodiesel from microalgae. Microalgae, also referred as third-generation oil, is a promising alternative feedstock to produce biodiesel. It can be easily grown in industrial reservoirs, municipal reservoirs, and open ponds without much land use requirement [68,69]. Besides, the production rate of algae oil is much higher (20–50%), where carbon dioxide is used as a carbon source and sunlight energy is used for oil accumulation [70]. Due to this, several researchers have been investigated extensively in harvesting algal oil. Despite the higher oil production rate exhibited by microalgae, conventional production using bioreactors are rather expensive and harvesting algal may require more energy input than supply [71]. Thus, the critical stage in developing microalgae biodiesel is the extraction of microalgae oil since it involves an extensive amount of chemicals and the dissociation of lipid from the algae oil is technically difficult [72]. Therefore, the oil extraction technology must improve for large scale productions. Table 4 shows the types of microalgae biomass used to produce biodiesel.

Table 4
Third-generation biodiesel feedstock for biodiesel production [73,74].

Feedstock	Lipid content, wt%
Chlorella protothecoides	23–55
Chlorella Vulgaris	25–63
Botryococcus braunii	25–75
Chlorella sorokiana	22–35
Schizochytrium sp.	50–77
Nitzschia laevis	45–47
Parietochloris incise	35–62
Crypthecodium cohnii	20–56
Nannochloropsis oculate	31–68
Monodus subterraneus	32–39
S. obliquus	33–55

3. The recent development of solid catalysts in biodiesel production

Catalyst is generally defined as a substance that influences the rate of a chemical reaction without being consumed by the reaction. An active catalyst accelerates the rate of reaction with a small quantity and the structure remains unchanged after the reaction [75]. Biodiesel is produced from the transesterification reaction between triglycerides and methanol under the presence of a catalyst. The catalyst reported in the literature can be classified as acid, base, and bio-based catalyst [76]. Fig. 1 illustrates the classification of catalysts used in biodiesel production. The utilisation of base transesterification requires a highly purified feedstock with low FFA content because high FFA contents could stimulate soap formation associated with alkali metal from base catalyst with the presence of water, which reduces the ester yield and affect the quality of the product [77,78]. Hence, homogeneous acid catalyst such as HCl and H_2SO_4 is used as an alternative as they are less sensitive to FFA and water. However, it is difficult to separate homogeneous catalysts from the reaction product and it discharges a large volume of wastewater from the neutralization treatment process. With such downfalls, heterogeneous solid catalysts can serve as an excellent substitution for homogeneous catalysts. Heterogeneous catalysts can be divided into solid acid (e.g., zeolites, heteropoly acids) and solid base (e.g., alkali metal oxide, mixed metal) [79]. Increasing the pore size and surface area of the catalyst support could improve the conversion as it promotes a higher number of accessible active sites for triglycerides to react and resulting in a better product yield [19]. Unfortunately, heterogeneous catalysts are easily deactivated in the presence of sulphur impurities. Reaction with the bulky oil molecules may clog the porous catalyst [80].

Recently, numerous studies have been explored by utilizing waste materials as potential raw material or catalyst in biodiesel production. Vargas et al. [81] utilised biomass fly ashes as solid waste material for catalyst preparation. The catalytic performance of fly ashes was evaluated in the production of biodiesel using a blended mixture of refined palm oil and waste cooking oil feedstock and a maximum biodiesel yield of 96% was achieved using biomass fly ashes as catalyst material. Besides fly ashes, carbon-based heterogeneous acid catalyst was synthesised from bamboo and prepared via partial-carbonisation and sulphonation with an initial activation using phosphoric acid [82]. The carbon-based heterogeneous catalyst has a relatively large surface area of 1208 m^2/g and mild acidity of 1.28 mmol/g after carbonisation at 350 °C for 2 h and sulphonation at 105 °C for 4 h. The highest biodiesel yield of 97.3% was achieved under the optimal esterification reaction conditions at 60 °C with 9:1 (mol:mol) methanol to oil and 10 wt% catalyst over 180 min in batch reactor. After the fourth cycle, the biodiesel yield dropped to 83.7% due to the leaching of sulphonic acid ($-SO_3H$). Therefore, the major challenges in developing heterogeneous solid catalysts involve low recovery, reactivation, and reusability of catalysts after several reaction cycles with substantial loss in catalytic activity.

Since then, the applications of magnetic catalyst in biodiesel production have gained considerable attention to many researchers. Magnetic catalyst has high surface area, high stability, excellent recovery and reusability. The catalyst can be separated and recovered easily by using magnetic force. The catalysts can be reused multiple times with little drop in catalyst activity [83]. Oladipo et al. [84] prepared a KF/eggshell-Fe_3O_4 catalyst using impregnation-calcination and co-precipitation methods. The catalyst synthesised possesses a high surface area of 128 m^2/g with a mesoporous structure. The catalyst has a large pore width of 3.24 nm. It offers better surface contact opportunity with reactant to achieve a higher biodiesel yield. By using neem oil as the feedstock, the KF/eggshell-Fe_3O_4 produced 94.5% of biodiesel. Under optimised reaction conditions, a maximum biodiesel yield of 97% was attained. Furthermore, a biodiesel yield of 97% was achieved from the transesterification of waste cooking oil using the same catalysts.

In another work, Liu et al. [85] converted sawdust into a magnetic porous carbonaceous (MPC) heterogeneous acid catalyst via fast pyrolysis and sulphonation processes. The porous magnetic heterogeneous acid catalyst has a surface area of 296.4 m^2/g. The presence of Fe improved the formation of the porous structure and facilitates the release of volatile materials. The catalyst with an acid strength of 2.57 mmol/g was reused for five times with little deterioration in the catalytic activity, which indicated the excellent stability of the magnetic porous carbonaceous (MPC) sulphonic acid group.

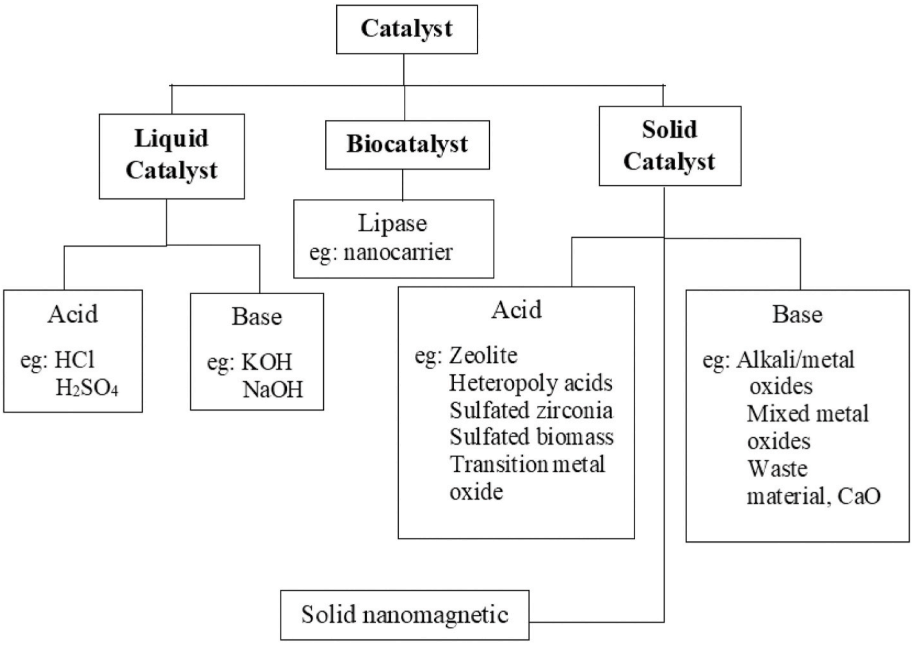

Fig. 1. Classification of catalyst.

4. Magnetic solid acid catalyst for esterification and transesterification reaction

Although heterogeneous acid catalysts can be recovered from filtration or centrifugation methods, investigations on the catalyst recovery, reusability and stability are still limited. Thus, many researchers have synthesised magnetic solid acid catalyst by exploiting its ease of separation from a reaction mixture by using an external magnetic force and high catalyst recovery rate.

4.1. Magnetic composite solid acid catalysts

Recently, much efforts have undertaken in developing porous composite catalysts material with high catalytic activity, selectivity, and deactivation resistance. Gardy et al. [86] investigated the transesterification of waste cooking oil (WCO) using the SO_4/Fe–Al–TiO_2 catalyst. The alumina was coated with TiO_2 and iron oxides by co-precipitation and calcination methods. The calcination temperature was found to induce iron phase transition with the formation of hematite, FeAl–TiO_2. The FeAl–TiO_2 prepared was dispersed in dry toluene before chlorosulphonic acid was added and calcined at 400 °C. The resultant catalyst has a high acid loading, mainly attributed to the presence of Brønsted acid sites. The optimum reaction conditions for transesterification reaction were found to be 2.5 h at 90 °C with 3 wt% catalyst and 10:1 of methanol: WCO. A high biodiesel yield of 95.6% was attained. It was reported that a maximum biodiesel yield of 95% was attained up to 10 consecutive reactions, further strengthen the fact that SO_4/FeAl–TiO_2 has good stability and recyclability.

On the same note, Zhang et al. [87] used Brønsted-Lewis acid bifunctional ionic liquid to synthesise Fe_3O_4@SiO_2 magnetic catalyst from a solvothermal method and modified Stöber method. Under the intensification of ultrasonication vibration, tetraethyl orthosilicate was added and functionalized with hydrochloric acid (HCl). Furthermore, lewis acid monofunctional ionic liquid Fe_3O_4@SiO_2 magnetic was also synthesised using (3-chloropropyl) trimethoxysilane (CPMS) and imidazole. The FTIR bands at 580 and 1088 cm^{-1} were assigned to the presence of Fe–O and Si–O–Si groups, respectively, which indicated the functionalization of Fe_3O_4@SiO_2 catalyst with acidic ionic liquid. Meanwhile, the S=O stretching vibration at 1180 and 1040 cm^{-1} indicated the presence of -SO_3H groups within the catalyst. In the context of catalytic performance, a high biodiesel yield of 93.7% was also demonstrated from direct transesterification of non-edible *Koelreuteria integrifoliola* oil at 160 °C for 10 h.

Similarly, Mohammad Fauzi et al. [88] prepared 1-butyl-3-methylimidazolium tetrachloroferrite ([BMIM][$FeCl_4$]) by using ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) and ferric chloride hexahydrate ($FeCl_3.6H_2O$). The catalyst was successfully yielded 83.4% of methyl oleate from oleic acid under the optimum reaction conditions of 0.003 mol catalyst, 22:1 methanol to oleic acid at 65 °C for 3.6 h. Wu et al. [89] also prepared a magnetic solid acid catalyst $S_2O_8^{2-}/ZrO_2–TiO_2–Fe_3O_4$, at different molar ratios of Zr/Ti (1/0, 3/1, 1/1 and 1/3) using co-precipitation and impregnation methods. The highest acidity of 598.6 μmol/g was found in the SZTF-3-1 catalysts and a high biodiesel yield of 98.5% were also achieved under the optimised reaction conditions of 50 °C, catalyst loading, 21.3 wt%, and methyl acetate: cotton seeds oil, 13.8 ml:1g in 10.8 h reaction. The catalyst has demonstrated good recyclability with a stable conversion performance.

4.2. Ionic acid functionalized magnetic solid acid catalysts

Wan et al. [90] incorporated an ionic liquid-based magnetic catalyst for a biodiesel production process. Firstly, Brønsted ionic liquid 1-(propyl-3-sulfonate)-3-(3-trimethoxysilylpropyl) imidazolium hydrogen sulfate [SO_3H-PIM-TMSP][HSO_4] was synthesised and denoted as ionic liquid (IL). Secondly, the magnetic Fe_3O_4 microsphere was synthesised via the solvothermal method. The novel FSS-IL catalyst consisted of both good magnetism of 13.2 emu/g and high surface area of 175 m^2/g. The catalysts exhibited a high biodiesel yield of 93.5%. Besides, the catalyst can be recycled for several reactions without losing much of its activity. In another work of Li and Liang [91], they prepared a new magnetic solid acid catalyst with a precursor derived from (3-aminopropyl) trimethoxy-silane and functionalized with ionic liquid. The catalyst has an acidity of 1.5 mmol/g, which is considerably lower than the theoretical acid density of 2.5 mmol/g. This could be due to the improper immobilization of IL on the magnetic core. With such immobilization of bulky IL molecules on the magnetic core, the surface area of catalyst decreased from 245 m^2/g (magnetic core) to 92 m^2/g. Despite the decline in surface area, the catalyst was still exhibited relatively high biodiesel yield of 98.9% under the reaction conditions of 50 mg catalyst loading, 2.91g methanol: 5g waste oil at 70 °C for 9 h.

Zhang et al. [92] investigated the catalytic performance of magnetically acidic poly catalysts for biodiesel production where the catalyst, FnmS-poly, was functionalized with trifluoromethanesulphonic acid. The catalyst has a large surface area of 128.1 m^2/g, excellent magnetism of 12.4 emu/g, and high acidity of 2.14 mmol/g. In esterification of oleic acid, a high conversion performance of 95.3% was obtained under the mild reaction conditions of 17:1 methanol: oleic acid, 4 wt% catalyst loading at 75 °C for 3 h reaction. Meanwhile, biodiesel yield of 91.7% was achieved via direct conversion of *Euphorbia lathyris* L. seed oil. After five cycles of transesterification, the catalyst shown excellent catalytic stability with an average biodiesel yield of 87.5%. Table 5 shows a summary of the magnetic composite based acid catalyst utilised for biodiesel production.

4.3. *Carbon supported magnetic solid acid catalyst*

Apart from porous composite based catalysts, carbon-supported magnetic acid catalysts have also attracted significant interests in recent years. It is cost-effective and environmental-friendly. Furthermore, previous works have shown that the magnetic carbon based catalysts have a higher surface area than non-magnetic carbon based catalysts. D'Souza et al. [93] investigated the direct conversion of WCO using graphene supported magnetic solid acid catalysts. The graphene oxide and Fe_2O_3 (hematite) nanocomposite were mixed with concentrated sulphuric acid using sonication technique. The FTIR band at 1040 cm^{-1} corresponded to the presence of S═O symmetric stretching vibration in the sulfonated catalysts. The catalyst synthesised has an acidity of 0.46 mmol/g. With an ethanol to oleic acid ratio of 12:1 and 5 wt% of catalyst loading, near complete conversion was achieved at 100 °C within 4 h. The presence of sulphonic acid groups and Fe_2O_3 compound improved the catalytic activity as the high surface area of the catalysts promoted a better accessibility of the reactants within the porous structure. About 72% of biodiesel yield was successfully attained using the graphene supported magnetic solid acid catalysts.

Other than the graphene based magnetic catalysts, Rechnia-Gorący et al. [94] prepared activated carbon magnetic solid acid catalyst for the transesterification of rapeseed oil to biodiesel. The activated carbon was prepared from ash wood sawdust. The activated carbon synthesised was activated with CO_2 after impregnated with calcium chloride solution ($CaCl_2$), followed by demineralization of HCl. By using the pre-treated activated carbon as template, acidic activated magnetic carbon catalyst was prepared via several chemicals modification methods including concentrated H_2SO_4, sodium sulfite (Na_2SO_3), 4-aminobenzenesulphonic acid, phosphoric acid through impregnation method, and oxidation with sulphuric acid/nitric acid mixture. The modification of sawdust by 4-aminobenzenesulphonic acid at room temperature was the most effective method for carbon sulphonation and resulted in an acidity of 0.86 mmol/g. Furthermore, in comparison to the commercial acid catalyst (Amberlyst-15), the carbon-based catalysts have a larger number of sulphonic groups. The catalytic performance of all catalysts synthesised in transesterification of rapeseed oil was evaluated at 130 °C. Compared to the commercial catalyst with a biodiesel yield of 50%, a higher FAME yield of 60% was obtained from acidic activated magnetic carbon catalysts.

In additional, Zhang et al. [95] prepared a novel magnetic acid catalyst from glucose for biodiesel production. The magnetic core Fe/C was synthesised from hydrothermal precipitation and pyrolysis methods. The magnetic core Fe/C was recoated hydrothermally with glucose and undergoes pyrolysis reaction at high temperature. Lastly, the thermally degraded magnetic carbon catalysts were directly sulfonated with concentrated sulphuric acid. From the results, AC-600-SO_3H@Fe/C catalyst exhibited a high acidic of 2.79 mmol/g and strong magnetism of 14.4 Am^2/kg. The highest biodiesel yield of 90.5% was achieved under optimised conditions with methanol to oil of 24:1 and 10 wt% catalyst loading at 200 °C for 10 h. The catalyst was recycled and reused for three times with little catalyst loss. The recovery rate achieved was as high as 96.3%.

Next, a new magnetic cellulose microsphere (MCM) heteropoly-acid catalyst was developed by Han et al. [96]. The cotton was regenerated into cellulose microsphere by modification and grafting using epichlorohydrin and triethylenetetramine (TETA). The regenerated cellulose microsphere was loaded with Fe_3O_4 by in-situ co-precipitation, followed by immobilization of heteropolyacid, HPW. The prepared magnetic acid catalyst, MCM-HPW was evaluated for tranesesterification of *Pistacia Chinensis* seed oil to biodiesel. It demonstrated high conversion yield of 93.1% under the reaction conditions of 15 wt% catalyst loading, methanol to the oil of 10:1 at 60 °C for 80 min. The catalysts were separated from the reaction mixture using a magnet and reused for at least four times.

Wang et al. [97] synthesised a carbonaceous bifunctional magnetic heterogeneous acid catalyst, Zr-CMC-SO_3H@3Fe–C_{400} catalyst from chelation and calcination of Fe metal ion. The Fe-solid was chelated with metal Zr ion and sulfonated using concentrated sulphuric acid. The resultant catalyst has a high acid content of 8.84 mmol/g and a weak magnetism of 6.20 Am^2/kg. The Zr-CMC-SO_3H@3Fe–C_{400} catalyst achieved a maximum yield of 97.39% for the esterification of oleic acid. The catalyst was separated by a magnet and reused ten times with an average biodiesel yield of more than 90%. For the transesterification reaction of *Jatropha* oil, a biodiesel yield of 95.4% was achieved at 90 °C for 4 h with 12:1 of methanol to oil and 9 wt% catalyst loading. The catalyst was recycled and reused up five cycles. The acid value of catalyst was reduced from 7.2 mgKOH/g. to 0.7 mgKOH/g.

Table 5
Esterification and Transesterification reaction using the magnetic solid acid catalyst in biodiesel production.

Catalyst	Magnetism, emu/g	Reaction conditions					Yield, %	Recyclability	References
		Feedstock	Temperature, °C	Alcohol: Oil, molar mass	Reaction time, h	Catalyst loading, wt%			
SO_4/Fe–Al–TiO_2	0.65	WCO	90	10:1	2.5	3	95.6	>90% after 10 cycles	[86]
Ionic liquid Fe_3O_4@SiO_2	22.1	*Koelreuteria integrifoliola* oil	160	40:1	10	10	93.7	87.8 after 6 cycles	[87]
[BMIM][$FeCl_4$]	–	Oleic acid	65	22:1	3.6	0.003mol	83.4	-65% after 6 cycles	[88]
$S_2O_8^{2-}$/ZrO_2–TiO_2–Fe_3O_4	21.0	Cottonseeds oil	50	13.8 mg:1g	10.8	21.3	98.5	85% after 14 cycles	[89]
[SO_3H-PIM-TMSP] [HSO_4]	13.2	Oleic acid	100	60 mmol:10 mmol	4	0.2g	93.5	87.4% after 6 cycles	[90]
Ionic liquid (3-aminopropyl) trimethoxysilane	–	Waste oil	70	2.91g:5g	9	50 mg	98.9	97.3% after 6 cycles	[91]
Acidic poly (ionic liquid)	12.4	Oleic acid	75	17:1	3	4	95.3	87.5% after 5 cycles	[92]

In another study of Chang et al. [98], a novel magnetic mesoporous carbon sphere (MMCS−SO_3H) acid catalyst was synthesised. The mesoporous carbon sphere was prepared by using resorcinol, formaldehyde solution, and triblock copolymer Pluronic. Magnetic mesoporous carbon sphere (MMCS) was prepared from the addition of ferric chloride hexahydrate followed by sulphonation reaction with *p*-toluenesulphonic acid. The catalyst has an acidity of 1.08 mmol/g and achieved a high conversion of 95% at 100 °C with methanol to oil ratio of 30:1 and 5 wt % catalyst loading in 6 h reaction. The results showed that it can be recycled and reused with minimal loss in activity. Thus, this carbon magnetic acid catalyst can be used as a potential catalyst alternative for biodiesel processing.

Biomass-derived solid catalysts are commonly used in a wide range of applications because they are considered as non-corrosive, non-toxic, and environmentally friendly. Wang et al. [99] discovered the application of biomass supported magnetic sulphonic acid catalyst in biodiesel production using biomass-derived chitosan. The FCHC–SO_3H, the catalyst was co-precipitated and sulfonated with *p*-toluene sulphonic acid monohydrate. The synthesised catalyst was used to catalyse transesterification of oleic acid. A high yield of 96.7% was achieved under an optimum reaction conditions of 15:1 methanol to oil with 4 wt% catalyst loading at 80 °C for 3 h. The presence of sulphonic groups such as -SO_3H and NH_3^+ sites on the catalyst improved its efficiency in producing biodiesel. The catalyst was able to recycle up to five cycles with a slight reduction in catalytic activity.

In another study by Zhang et al. [100], magnetic carbonaceous acid catalysts were synthesised from the hydrolysate of *Jatropha* hulls. The JHC-12-600-$SO_3H@Fe_3O_4$ catalyst was prepared from hydrothermal precipitation, carbonisation, and sulphonation using sulphuric acid. The catalyst consists of aromatic carbon bonded active groups such as hydroxyl (–OH), carboxyl (-COOH), and -SO_3H with a high acidic of 2.69 mmol/g and magnetism of 40.3 Am^2/kg. From the transesterification of *Jatropha* oil, an average of 95.9% biodiesel yield was achieved at the optimum conditions of methanol to oil, 18:1, and 7.5 wt% catalyst loading at 180 °C for 7.5 h with a catalyst recovery rate of 94.3%.

Lastly, Zhang et al. [101] prepared magnetic carbonaceous acid (C–SO_3H@Fe/JHC) catalyst from *Jatropha*-hull hydrolysate for the production of biodiesel. The C–SO_3H@Fe/JHC catalyst was prepared via the hydrothermal reaction between *Jatropha*-hull hydrolysate, $FeCl_3$, and urea. The pyrolyzed catalyst was recoated with *Jatropha*-hull hydrolysate and sulfonated with concentrated H_2SO_4. The C–SO_3H@Fe/JHC catalyst exhibited high catalytic activity with a biodiesel yield of 92.44%. The authors deduced that a catalyst with a smaller size has a large surface area and promotes a better contact frequency between the reactant and catalysts. Besides, the catalyst has a magnetism of 11.2 Am^2/kg and a high acidic of 2.96 mmol/g. The solid magnetic acid catalyst attained an average biodiesel yield of 90.3% with five reaction cycles. Table 6 shows a summary of the carbon-based magnetic acid catalyst utilised for biodiesel production.

4.3.1. Synthesis of magnetic particles

Magnetic particles can be prepared from various methods such as chemical, physical, and biological. Despite the high effectiveness of physical methods reported in the literature, the resultant catalysts generally suffer from poor particle size distribution. Chemical methods are the simplest and most efficient process, provided that the particle size and shape can be regulated by adding a base chemical in the co-precipitation of Fe^{2+} and Fe^{3+} [103]. The synthesis of magnetic particles is usually governed by the type of salt used, chemical ratio and pH. A conventional synthesis method of magnetic catalysts involves impregnation of ferrite ion followed by carbonisation process. The carbonised particles are functionalized using an acid or base solution. The ferric chloride ($FeCl_3$) is hydrolysed to ferric (III) oxide-hydroxide (FeO(OH)) before transforming into anhydrous form [104]. Subsequently, the impregnated sample is carbonised under higher temperature to produce ferric (III) oxide, Fe_3O_4, or also known as magnetite. The Fe compounds found in Fe_3O_4 and FeO(OH) were found to enhance the pore formation during the carbonisation process. The chemical methods reported in the literature include chemical co-precipitation, sol-gel, hydrothermal, microwave, and microemulsion.

4.3.1.1. Chemical co-precipitation method. Co-precipitation method is the most commonly used method in preparing magnetic particles. With co-precipitation, the size of magnetic particles and properties can be easily controlled (either Fe_3O_4 or γ-Fe_2O_3). The preparation step generally involves addition of ferric, Fe(III) and ferrous, Fe(II) ions to a base solution in a certain molar ratio under room temperature or certain temperature [105]. The chemical reaction is written as follows:

$$Fe^{2+} + 2Fe^{3+} + 8OH– \ Fe_3O_4 + 4H_2O$$

Usually, magnetic particles are preferred in aggregated form due to the high surface area to volume ratio and its propensity to reduce its surface energy. The super-paramagnetic iron oxide particles were prepared from precipitation method using $FeCl_3$ and $FeCl_2$ [106]. The synthesised magnetite particles were found to be spherical and the

Table 6

Esterification and Transesterification reaction using the carbon-supported magnetic solid acid catalyst in biodiesel production.

Catalyst	Magnetism, emu/g	Reaction conditions					Yield, %	Recyclability	References
		Feedstock	Temperature, °C	Alcohol: Oil, molar ratio	Reaction time, h	Catalyst loading, wt%			
Graphene oxide-Fe_2O_3	–	Oleic acid	100	12:1	4	5	∼100	>80% after 7 cycles	[93]
		WCO	90		6		70	1.5% after 4 cycles	[94]
AC-600-SO_3H@Fe/C	14.4	*Jatropha oil*	200	24:1	10	10	90.5	>90% after 3 cycles	[95]
MCM-HPW	–	*Pistacia chinensis* seed oil	60	10:1	80 (min)	15	93.1	80.7% after 4 cycles	[96]
Zr-CMC-$SO_3H@3Fe–C_{400}$	6.2	*Jatropha oil*	90	12:1	4	9	95.4	>90% after 10 cycles	[97]
MMCS-SO_3H	–	Oleic acid	100	30:1	6	5	95	∼90% after 5 cycles	[98]
FCHC–SO_3H	19.8	Oleic acid	80	15:1	3	4	96.7	84.3% after 5 cycles	[99]
JHC-12-600-$SO_3H@Fe_3O_4$	40.3	*Jatropha oil*	180	18:1	7.5	7.5	95.9	94.3 after 5 cycles	[100]
C–SO_3H@Fe/JHC	11.2	*Jatropha oil*	90	12:1	2	10	92.44	>85% after 10 cycles	[101]

diameter was estimated to be 8 nm from X-ray diffraction analysis. The study also showed that type of base solution (ammonia, methylamine, and sodium hydroxide), pH, cations, and Fe^{2+}/Fe^{3+} ratio are the key factors in affecting the yield in this reaction. In additional, Zhang et al. [107] synthesised Fe_3O_4 nanoparticles from $FeCl_2.4H_2O$ and $FeCl_3.6H_2O$. The particles loaded in carbon nanotubes were firstly functionalized via oxidation of nitric acid. The saturation magnetization (Ms) of the particles was determined as 6.5 em/g and 7.52 emu/g with a diameter of 6 nm and 10 nm, respectively. The Ms of pure Fe_3O_4 particles, for 6 nm and 10 nm were recorded to be 65.257 emu/g and 101.24 emu/g, respectively [108]. The reduction in magnetism may be attributed to the infusion of carbon nanotubes in magnetite preparation.

4.3.1.2. Sol-gel method. The sol-gel method involves hydroxylation and condensation of molecular precursors in solution. A 'sol' of nanometric particles were dried by removing the solvent or by chemical reaction (condensation and inorganic polymerization) that lead to a three-dimensional metal oxide network known as wet gel [109]. The typical solvents used are water and precursor (e.g., metal alkoxides) that soluble in an acid or a base solution. In the base reaction, a colloidal gel is produced. Whereas in the acid reaction, a polymeric gel is formed [110]. The reaction is typically carried out under room temperature. To obtain a crystalline form, heat treatment is usually required.

Moreover, the preparation of magnetic particle using this method is strongly influenced by pH, concentration of precursor, reaction temperature, and properties of gel [111]. From this preparation method, the particle size can be easily controlled with excellent phase homogeneity and the embedded molecules have high catalytic stability. In the previous study, the magnetite particles were successfully prepared from the sol-gel method with annealing of non-toxic ferric chloride and ethylene glycol at 200–400 °C [112]. The characterization result indicated that the annealing temperature controlled the particle size of Fe_3O_4 and the particle size of Fe_3O_4 nanoparticles was calculated in a range of 2–25 nm. Unfortunately, this method suffers from contamination of the final product with volatile matters and post-treatment of the final products is required [113]. Besides, the weak bonding and high permeability in this method impede its effectiveness.

4.3.1.3. Hydrothermal method. The hydrothermal method offers an excellent balance in the size and shape of the magnetic particles [114]. The hydrothermal method is also called a solvothermal method, where it produces ultrafine particles. The hydrothermal reaction is usually performed in a reactor or autoclave at high reaction temperature ranges from 130 to 250 °C and under high pressure from 0.3 to 4 MPa. The internal reaction pressure is determined autogenously from the temperature and the volume of the solvent added in the autoclave. Fang et al. studied the microstructure and magnetic properties of $Sn_{1\text{-}x}Fe_xO_2$ with different proportions of $x = 0.01$, 0.05, and 0.10 nanoparticles prepared via hydrothermal method [115]. From the X-ray diffraction (XRD) result, it was revealed that the samples have a pure tetragonal phase with spherical shape and the particle size decreased with an increase of Fe content. The particle diameters were determined as 5–6 nm. The magnetism value also showed that the Fe doped SnO_2 particles have paramagnetic behaviour. The decreasing trend of magnetism was observed with an increase of Fe concentration, attributed to the anti-ferromagnetic force. The only downfalls of using this method in preparing magnetic particles are the use of high temperature and pressure.

In a study conducted by Liu et al. [116], cellulose-based composites with Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3 particles were successfully synthesised using the microwave-hydrothermal method at 180 °C for 45 min. Both calcination temperature and atmosphere were varied and altered during the calcination process. The Fe_3O_4 catalyst was obtained from the furnace with nitrogen gas (N_2) flow at 300 and 500 °C for 3 h. Meanwhile, γ-Fe_2O_3 and α-Fe_2O_3 phases were achieved at 300 and 500 °C for 3 h in the vacuum and air furnace, respectively. Besides, magnetism analysis also showed that both Fe_3O_4 and γ-Fe_2O_3 exhibited super-paramagnetic characteristics with good absorption performance.

4.3.1.4. Microwave method. Microwave technology has obtained a great interest in recent years. It has been employed extensively for chemical preparation and material synthesis since 1986 [117]. By using this technique, the reaction parameter can be easily controlled and uniform particles size/shape can be obtained. However, homogeneous nucleation of magnetic particles is the major disadvantage of using this method. It was reported previously that ultra-fine particles obtained from microwave heat have a high electrochemical performance due to the uniform arrangement and size of the particles [118]. The nano-sized magnetic particles also exhibited super-paramagnetic characteristics with potential applications in multi-field. In the context of heating time, a shorter reaction time generally produces a smaller magnetite particle size with the crystal lattice. Li et al. [119] prepared biomass-derived magnetic ferric oxide/SO_4^{2-}, acid catalyst from levulinic acid via pyrolysis process. To obtain magnetic ferric oxide/SO_4^{2-} catalysts, the corn straw biomass was firstly sulfonated and carbonised. The magnetic iron oxide particles, MIO were then prepared using Na_2SO_3, ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), and $FeCl_3{\cdot}6H_2O$. The biomass precursor and MIO were mixed with a sulphuric acid solution to obtain MIO/SO_4^{2-} B-BSAC. A maximum yield of 23.17% was achieved from the catalysts synthesised in this study.

4.3.1.5. Microemulsion method. Microemulsion is a thermodynamically stable of two otherwise immiscible phases in the presence of added surfactants. The surfactant compounds create a monolayer between the water and oil with the hydrophilic head at the aqueous phase and hydrophobic tail dissolved in the oil [120]. For the synthesis of magnetite particles, nano-emulsion containing Fe source and NaOH were firstly mixed before removing the surfactant using acetone and washing with ethanol. This method is more convenient compared with other methods because it only requires simple laboratory equipment. It has good control over the particle sizes under relatively mild reaction conditions. It offers a high specific surface area with the formation of crystalline structures [121]. Particles produced by microemulsion method was found to be small-sized with the typical range of 2–3 nm and high magnetization of 81 emu/g. Nonetheless, the selection of surfactant plays an important role in this preparation method. Kekalo et al. [122] synthesised magnetic iron particles under an inert atmosphere. The magnetic iron particles were obtained from the reaction between $FeCl_3$ and $NaBH_4$ in droplets of water. The microemulsion conducted using octane with cetyl trimethylammonium bromide and butanol as surfactants. From the results, Fe core particles retained their magnetic and physicochemical properties under an inert atmosphere. The surfactant can be divided into anionic, cationic, and nonionic surfactants [123]. On the other hand, the major disadvantage of this method is the side effect of surfactant residues on the product properties and its difficulty in scaling up.

5. Magnetic solid base catalyst for transesterification reaction

Despite the distinct advantages of heterogeneous base catalysts in the separation of catalysts, investigation on catalytic performance and stability are still scarce. Magnetic solid base catalyst possesses great potential for easy catalyst separation with magnetic force, which reduces the catalyst loss and improves its post-reaction recovery. Besides, the small particle size with a high surface area also allows better interaction with reactant and improves biodiesel conversion.

5.1. *Magnetic composite solid base catalysts*

Xie and Wan [124]. used the base ionic liquid to functionalized magnetic Fe_3O_4@HKUST-1 composite for biodiesel production. The

Fe_3O_4@HKUST-1-ABILs catalyst was prepared with amino-functionalized basic IL (ABIL-Im) from the solvothermal method. The Fe_3O_4@HKUST-1 composite was prepared via the Layer-by-Layer assembly method and functionalized with basic IL ABIL-Im. The solid base catalysts have a super-paramagnetic property and high magnetization of 32.84 emu/g. In the context of catalytic performance, the catalyst achieved a biodiesel yield of 92.3% under the reaction conditions of 30:1 methanol: oil, 1.2 wt% catalyst loading at 65 °C for 3 h. Also, Zhang et al. [101] performed a direct conversion to biodiesel using magnetic Na_2SiO_3@Fe_3O_4/C catalyst using ultrasonic irradiation and magnetic stirring. The catalyst was synthesised using activated carbon as a precursor. Fe_3O_4, magnetic Fe_3O_4/C was introduced into the activated carbon by calcination. The prepared particles were mixed with sodium silicate solution to produce Na_2SiO_3@Fe_3O_4/C catalyst. In this work, the transesterification reaction was performed under two methods: ultrasonic irradiation and magnetic stirring. From the results, biodiesel yield of 96.3% (ultrasonic irradiation) and 94.9% (magnetic stirring) was successfully achieved under the reaction conditions of methanol to the oil of 7:1, 5 wt% catalyst loading at 65 °C for 100 min. From the ultrasonic irradiation method, an optimised biodiesel yield of 97.9% was achieved. Encouraging by such positive results, Jatropha oil was also used to produce biodiesel and a comparably high biodiesel yield of 90.7% was attained. In another study conducted by Xie et al. [125], magnetic Fe_3O_4/MCM-41 composite with sodium silicate was prepared via co-precipitation method. Stober method was used for silica coating. The Fe_3O_4/MCM-41 synthesised has a large surface area of 443.7 m^2/g. After loading with sodium silicate, the surface area of Fe_3O_4/MCM-41/ECH/Na_2SiO_3 catalyst reduced to 54.3 m^2/g. The bulk particle size of sodium acetate increased considerably, which leads to a reduction in magnetism from 38.2 emu/g to 31.8 emu/g. However, the catalyst was still able to achieve a high biodiesel yield of 99.2% under 25:1 of methanol to oil, 3 wt% catalyst loading at 65 °C for 8 h.

Ambat et al. [126] produced nano-magnetic potassium ceria from co-precipitation, impregnation, and calcination methods. Various concentration of potassium impregnated Fe_3O_4–CeO_2 was investigated. It was found out that 25 wt% potassium impregnated Fe_3O_4–CeO_2 nano-catalyst has a surface area of 72.84 m^2/g and magnetism of 0.75 emu/g. Under the optimum reaction conditions of 4.5 wt % catalyst amount and 7:1 of methanol to oil at 65 °C for 120 min, a maximum of 96.13% yield was achieved. Salimi and Hosseini [127] prepared ZnO/$BiFeO_3$ magnetic catalyst via co-precipitation method for biodiesel production from edible oil. From the results, the basic strength displayed strongest for the weakest indicator and weakest for the strongest indicator. The range of basic strength was reported in between 9.3 and 15. Meanwhile, ZnO/$BiFeO_3$ magnetic catalyst super-paramagnetic property, evidenced by its magnetization value of 13.65 emu/g. The base strength analysis by CO_2-TPD concluded that the addition of ZnO enhanced the catalyst's basic sites and promote high catalytic activity for transesterification reaction. Under the optimum conditions of 15:1 of methanol to oil and 4 wt% catalysts, a high biodiesel yield of 95.43% was achieved at 65 °C for 6 h reaction. The catalysts were able to reuse after 5 cycles with an average yield of 92.08%. Bayat et al. [128] worked on magnetic nano-alumina prepared from co-precipitation and coating methods. The effect of different Al_2O_3/Fe_3O_4 mass ratios (0.2–2) in the transesterification reaction was studied. The result showed that an increase of the Al_2O_3/Fe_3O_4 mass ratio could decrease the catalytic performance due to the presence of large particle size, subsequently reduces the surface area. According to the DLS result, the Fe_3O_4 in Al_2O_3/Fe_3O_4 catalysts with a mass ratio of 0.5 has particle size of 193 nm. This allows the reactant to be easily accessible to the active sites during the reaction and a maximum yield of 99.1% was achieved under the methanol to oil ratio of 32:1, 5 wt% catalyst loading at 99.8 °C for 2.95 h. Kelarijani et al. [129] also prepared nano-magnetic catalysts for the transesterification of rapeseed oil. Li/Fe_3O_4 and Li/ZnO–Fe_3O_4 catalysts were prepared by using the sol-gel and impregnation methods. The magnetization value was found to be 58.2 and 24.6 emu/g, respectively. The transesterification reaction of rapeseed oil was conducted using the ultrasonic irradiation method. The highest yield of 99.8% was achieved for both Li/Fe_3O_4 and Li/ZnO–Fe_3O_4 catalysts using 0.8% catalyst and methanol to oil of 3:1 at 35 °C for 35 min. Apart from high yield, the catalyst was successfully regenerated and reusable for several cycles. Table 7 shows a summary of the magnetic composite based base catalyst utilised for biodiesel production.

5.2. Supported magnetic solid base catalysts

A novel magnetic carbonaceous heterogeneous base catalyst, Na_2SiO_3@Bi/JRC, was synthesised by Zhang et al. [101]. Jatropha hydrolysis residue was used as carbonaceous support and active groups were loaded by the hydrothermal method. The heterogeneous magnetic base catalyst has a strong magnetism of 15.0 Am^2/kg and high basicity with 3.24 mmol/g. The *Jatropha* oil was transesterified with Na_2SiO_3@Bi/JRC catalyst. It achieved a high yield of 96.7%, and the catalyst was recycled at least 3 times with a minimal loss in its activity. Liu et al. [131] synthesised an efficient magnetic solid base catalyst derived from bamboo charcoal for biodiesel production. The in-situ-impregnation-calcination method was used to prepare the solid magnetic base K/BC-Fe_2O_3 catalyst. The magnetization value was reported as 35.4 emu/g after calcination at 500 °C. After calcination at 700 °C, the magnetism was subsequently reduced to 13.4 emu/g due to phase transformation into α-Fe_2O_3. The magnetic base catalyst has a surface area of 28.7 m^2/g, and the catalyst's basic active sites can be easily accessed for transesterification reaction. Hence, the highest biodiesel yield of 98% was attained under optimised reaction conditions with 2.5 wt% catalyst loading, methanol to the oil of 8:1 at 60 °C for 1 h.

In another study, a magnetic catalyst KF/CaO–Fe_3O_4 was successfully developed by Hu et al. [132] using facile impregnation method. The magnetic catalysts were characterized by vibrating sample magnetometer (VSM) analysis to determine the magnetic property. The result indicated that the nano-magnetic base catalyst has ferromagnetic property and magnetically recoverable. Moreover, the catalyst has a porous structure with an average diameter of 50 nm. The base catalyst with 25 wt% potassium fluoride (KF) and 5 wt% Fe_3O_4 was calcined at 600 °C for 3 h. The catalyst exhibited a high catalytic activity with more than 95% yield at methanol to the oil ratio of 12:1 and 4 wt% catalyst loading at 65 °C for 3 h reaction time. The catalyst was reused up to 13 times, with a minimal loss in its activity. A similar approach of di-functional magnetic Fe–Ca oxide catalyst was developed by Ullah et al. [133]. The catalytic performance of magnetic Fe–Ca oxide catalysts in biodiesel production was evaluated using hemp oil. An in-situ co-precipitation method was conducted to synthesise the di-functional magnetic solid base catalyst, CaO-γ-Fe_2O_3, based on calcium hydroxide ($Ca(OH)_2$) and Fe_3O_4. The resultant porous catalyst has a relatively high magnetism of 45.6 emu/g. A maximum yield of 92.16% was achieved with 2.25% (w/w) catalyst loading at a constant reaction temperature of 60 °C with alcohol to the oil of 6:1 for 2 h. The catalyst was reused for more than four times without any drop in its activity. Shi et al. [134] successfully prepared magnetic nanoparticle CaO@Fe_2O_3 using sol-gel and precipitation methods for biodiesel production. The magnetic core was used as the supporting material for CaO. The catalytic activity of the catalysts with and without the addition of potassium nitrate, KNO_3 was evaluated and compared. From XRD analysis, the formation of hematite Fe_2O_3 and magnetic γ-Fe_2O_3 with CaO were observed, which denoted as CaO@hematite, and CaO@γ-Fe_2O_3 respectively. Besides, the CO_2-TPD basicity analysis indicated that CaO@hematite and CaO@γ-Fe_2O_3 have strong basic sites. In term of catalytic performance, CaO@γ-Fe_2O_3 has better catalytic activity than CaO@-hematite, Fe_2O_3 with 98.8% (soybean oil), 95.8% (palm oil) and 90.9% (castor oil), which corresponded to the basicity results. CaO@γ-Fe_2O_3 catalyst exhibited an average yield of 80% after four cycles and the reduction in biodiesel yield may due to the loss of basic sites during the reaction.

Table 7
Transesterification reaction using heterogeneous magnetic base catalyst in biodiesel production.

Catalysts	Magnetism, emu/g	Reaction conditions					Yield, %	Recyclability	References
		Feedstock	Temperature, °C	Alcohol: Oil, molar ratio	Reaction time, h	Catalyst loading, wt%			
Fe_3O_4@HKUST-1-ABILs	32.84	Soybean oil	65	30:1	3	1.2	92.3	>80% after 5 cycles	[124]
Na_2SiO_3@Fe_3O_4/C	48.6	Soybean oil	65	7:1	100min	5	96.3 (US) 94.9 (MS)	>79% after 3 cycles >73% after 2 cycles	[125]
Fe_3O_4/MCM-41/ECH/Na_2SiO_3	31.8	Soybean oil	65	25:1	8	3	99.2	85% after 5 cycles	[126]
Fe_3O_4–CeO_2	0.75	Rapeseed oil	65	7:1	120min	4.5	96.13	80.9% after 5 cycles	[127]
ZnO/$BiFeO_3$	13.65	Canola oil	65	15:1	6	4	95.43	92% after 5 cycles	[128]
Al_2O_3/Fe_3O_4	25.0	Waste cooking oil	35	3:1	35min	0.8	99.8	67% after 4 cycles	[129]
Li/Fe_3O_4 Li/ZnO–Fe_3O_4	58.2 24.6	Rapeseed oil	35	12:1	35min	0.8	99.8	60% after 3 cycles	[130]

Feyzi and Norouzi [135] worked on a novel magnetic Ca/Fe_3O_4@-SiO_2 nano-catalysts synthesised by sol-gel and incipient wetness impregnation methods. The Ca/(Fe_3O_4@SiO_2) catalysts were prepared via wetness impregnation method at a different weight percentage of Ca ranges from 2.0 to 10.0. The results showed that the catalyst with 8.0 wt % Ca/(Fe_3O_4@SiO_2) has a greater number of basic sites with the major desorption peak at 695 °C. The broad desorption peak ranges from 600 to 850 °C indicated the presence of strong basic sites. The magnetic catalyst exhibited a high biodiesel yield of 97% at the optimum conditions of methanol to oil of 15:1 at 65 °C for 5 h. Similarly, Zhang et al. [136] studied on Sr doping magnetic CaO parcel ferrite by a combination of co-preparation and calcination methods. The magnetic properties of CaO@ ($Sr_2Fe_2O_5$–Fe_2O_3) was determined by VSM analysis. The magnetism dropped significantly from 28.01 to 11.09 emu/g due to the presence of non-magnetic CaO on the surface. In comparison to the commercial CaO, a maximum biodiesel yield of 94.9% was achieved from the modified CaO@($Sr_2Fe_2O_5$–Fe_2O_3) at the reaction conditions of methanol to soybean oil of 12:1 and 0.5 wt% catalyst loading at 70 °C for 2 h. The biodiesel yield remained at approximately 89% after five cycles under the same reaction conditions. Tang et al. [137] produced a magnetic composite solid catalyst from impregnation and calcination methods. The effect of the Ca/Fe ratio, calcination temperature, and time on the catalytic performance were studied. The catalyst with Ca/Fe ratio of 5:1 exhibited the highest catalytic activity of 98.71% after calcined at 600 °C for 6 h. The biodiesel yield was retained more than 90% after five reaction cycles. In conclusion, the addition of magnetic particle promotes the diffusion of the solid catalyst and offers greater contact between the reactants and active sites, which contributes to the high biodiesel yield. Table 8 shows the summary of the carbon-based magnetic solid base catalysts utilised in biodiesel production.

6. Mechanism of magnetic solid catalyst catalysed esterification and transesterification reactions

The principal role of the acid catalyst in esterification reaction mainly acts as a proton donor vehicle, regardless of homogeneous or heterogeneous catalysts. Magnetite particles are employed as a catalyst in many organic reactions due to the Lewis acid character of Fe. In general, -SO_3H groups derived from a magnetic acid catalyst catalyses the esterification reaction. Three oxygen molecules accept the electrons from the sulphur to form -SO_3H electron-withdrawing (sulphonic) groups, which act as the Brønsted acid active sites [138]. The strong H^+ proton of the catalyst firstly attacks the oxygen in the carboxyl group during the esterification reaction. The alcohol molecule reacts with the activated carboxyl carbon through nucleophilic substitution. The intramolecular dehydration and hydrogen ion desorption lead to the formation of water molecules. Meanwhile, the presence of Lewis acid iron oxide (Fe–O) sites enhances the catalytic strength of Brønsted acids

Table 8
Transesterification reaction using the heterogeneous base catalyst in biodiesel production.

Catalyst	Magnetism, emu/g	Reaction conditions					Yield, %	Recyclability	References
		Feedstock	Temperature, °C	Alcohol: Oil, molar mass	Reaction time, h	Catalyst loading, wt%			
Na_2SiO_3@Bi/JRC	15.0	*Jatropha oil*	65	9:1	2	7	96.7	>85% after 10 cycles	[101]
K/BC-Fe_2O_3	13.4	Soybean oil	60	8:1	1	2.5	98	>94% after 4 cycles	[131]
KF/CaO–Fe_3O_4	–	Stillingia oil	65	12:1	3	4	95	>80% after 14 cycles	[132]
CaO-γ-Fe_2O_3	45.6	Hemp oil	60	6:1	2	2.25	92.16	>80% after 4 cycles	[133]
CaO-γ-Fe_2O_3	–	Soybean oil Palm oil Castor oil	70	15:1	3	2	98.8 95.8 90.9	80% after 4 cycles	[134]
Ca/Fe_3O_4@SiO_2	11.0	Sunflower oil	65	15:1	5	8	97	–	[135]
CaO@ ($Sr_2Fe_2O_5$–Fe_2O_3)	11.09	Soybean oil	70	12:1	2	0.5	94.9	86% after 5 cycles	[136]
Ca/Al/Fe_3O_4	6.34	Rapeseed oil	65	15:1	3	6	98.71	86% after 5 cycles	[137]

in a combined mechanism [139]. The Lewis acid sites polarize the alcohol hydroxyl (O–H) bond before accepting the protons from alcohol. The Brønsted acid sites combine with the carbonyl oxygen and activate the carbonyl carbon through a nucleophilic reaction with the formation of water molecules. The Brønsted and Lewis acid sites are regenerated to complete the catalytic cycle [140]. This mechanism results in the use of excess alcohol to drive the reaction forward, instead of reverse esterification reaction.

The magnetic base-catalysed transesterification mechanism is initiated with the generation of alkoxides species (M^+ OR^-) [141]. The alcohol in the reaction absorbed on the Lewis acid (Fe^{3+}) to form Brønsted acid. The affinity of alcohol groups towards sulfated Fe is higher due to its weak bonds [142]. The nucleophilic substitution of the acidic sites towards the alcohol will form methoxide anion. The carbonyl carbon of triglyceride forms an intermediate, which disassociates into alkyl ester and anion of the diglyceride [143]. The formed methoxide anion also known as Brønsted base sites. Whereas, the deprotonation of the catalyst by the diglyceride's anion regenerates the catalyst. This reaction cycle repeated with the diglyceride and monoglyceride molecules.

7. Future perspectives

In recent years, numerous research studies have investigated different types of heterogeneous catalysts and their potential in biodiesel production. To date, the investigation of biomass-based magnetic catalysts still limited. Intensive research works should be continued, especially on the effect of preparation method on the resulting textural properties of the biomass-derived magnetic catalyst. Hence, the waste biomass-based magnetic catalyst should be incorporated to avoid the usage of chemicals. Moreover, catalyst deactivation caused by leaching of active sites and catalyst reusability is remains an unsolved issue. Hence, methods in synthesizing waste biomass derived magnetic catalyst with high reusability and little leaching issue should be discovered. Besides, the catalyst preparation method with minimal steps is required to improve the feasibility of scaling up the process in future. Lastly, the experimental procedures or parameters should be investigated in detailed and optimised for the synthesis of a sustainable and environmentally friendly catalyst for biodiesel production.

8. Conclusion

Both catalysts and feedstock are the two major factors that affect the production costs of biodiesel. The commercially produced biodiesel mainly relies on the application of homogeneous catalysts in the transesterification reaction. Nonetheless, this homogeneous catalyst is nonrecyclable and requires additional downstream purification steps, which incurs additional penalties costs for the biodiesel production. Thus, the current review highlights the significance of magnetic catalysts in biodiesel production. The potential of feedstock for biodiesel production was discussed and different type of magnetic particle preparation methods was reviewed. Meanwhile, the application of magnetic acid and base catalysts were demonstrated with high catalytic activities and magnetism. Furthermore, heterogeneous magnetic catalyst generally offers an effective catalyst separation technique at a higher recovery rate compared to the conventional heterogeneous solid catalysts.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal conflicts that could have appeared to influence this work.

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