Arabian Journal of Chemistry (2022) 15, 104152

King Saud University

Arabian Journal of Chemistry

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REVIEW ARTICLE

Nanocatalysts for biodiesel production

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Received 1 April 2022; accepted 21 July 2022
Available online 26 July 2022

KEYWORDS

Biodiesel;
Magnetic nanocatalyst;
Esterification;
Waste cooking oils;
Transesterification

Abstract Biofuels are a class of clean fuels and promising for energy demand. Biodiesel is relatively costly, which limits the commercialization of the product. The waste edible oil and animal fats are raw materials for biodiesel production. This paper focuses on the catalytic production of biofuels and reviews the application of different catalysts to produce biodiesel from waste oils by using esterification and transesterification reactions. The reaction in the presence of nanocatalysts is carried out under mild operating conditions. Nowadays, magnetic nanocatalysts are preferred to bulk catalysts due to the absence of mass transfer resistance and fast deactivation as well as high recovery rate during the separation. Functionalized magnetic nanocatalysts are more attractive for biodiesel production. Further studies should do to develop highly active and selective nanocatalysts for industrial scale.

1. Introduction

Nowadays, fossil fuels are the prominent energy source in the world. The extra consumption of fossil fuels leads to global warming due to greenhouse gas emissions.

It is predicted that fossil sources will run out in near future. Therefore, more attentions are focused on finding renewable sources. It is expected that renewable energies will provide half of the global energy by 2040 and 70 % of greenhouse gases will be reduced (Banković-Ilić et al., 2017). Biodiesel is more significant among renewable fuels and has some advantages. Firstly, it. could be produced from low-cost sources such as waste animal fats and algal lipids. Also, biodiesel has a high flash point, low CO emission, and excellent lubricant properties. It is less toxic, biodegradable and does not contain sulfur-containing compounds (Banković-Ilić et al., 2017; Salimi and Hosseini, 2019).

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Furthermore, the waste oils from chickens processing plants and food industries could be used as raw materials and lead to get cheap biodiesel. Besides, this work helps reduce waste oil and fat disposal (Banković-Ilić et al., 2017; Salimi and Hosseini, 2019; Gardy et al., 2019).

In the modification of fuel composition for vehicles, biodiesel is used as fuel or as a fuel additive. In the chemical aspect, biodiesel is a mixture of fatty acid methyl esters (FAME) resulting from the reaction of methanol or ethanol with triglycerides or free fatty acids (FFAs) as shown in Fig. 1 (Salimi and Hosseini, 2019). Fig. 1(a) shows the mechanism of transesterification of triglycerides and Fig. 1(b) presents the esterification of fatty acids. The reaction could be done catalytically or non-catalytically.

There are numerous reviews about biodiesel production. Akia et al. published a review paper about the production of biodiesel from biomass by different methods (Akia et al., 2014). In this paper, they reported the production of liquid and gaseous fuels from biomass through different thermochemical and biological processes. They also reported the application of catalytic processes for biodiesel production from biomass. Ma and Hanna reported the production of biodiesel by four possible methods. The methods were direct blending, micro-emulsions, pyrolysis, and transesterification (Ma and Hanna, 1999). Also, Talebian-Kiakalaieh described the

https://doi.org/10.1016/j.arabjc.2022.104152
1878-5352

Nomenclature

Abbreviations	Full name		
FAME	fatty acid methyl esters	NPs	Nanoparticles
FFAs	Free Fatty Acids	MNP	Magnetic nanoparticles
RSM	response surface methodology	M/O	Methanol to oil
CNT	Carbon nanotube	APTMS	3-aminopropyl trimethoxysilane
MOF	Metal-organic frameworks	FAEE	Fatty acid ethyl esters

novel processes for biodiesel production. The catalytic reactions for biodiesel production were included in this paper (Talebian-Kiakalaieh et al., 2013).

The paper mainly focuses on biodiesel production by nanocatalysts and their types used in this process. However, at the beginning of the paper, the different bulk catalysts used in biodiesel productions have been surveyed. Then, the nanocatalyst-assisted approaches for biodiesel production were described and the role of nanocatalysts in biodiesel production was discussed. In addition, the mechanism for biodiesel production from oils over the nanocatalysts has been illustrated. The nanocatalysts were investigated in both categories of magnetic and nonmagnetic nanocatalysts and their advantages and disadvantages of them were discussed.

2. Catalysts in biodiesel production

Generally, the catalysts used in chemical reactions are classified into two types homogeneous and heterogeneous catalysts. Both homogeneous and heterogeneous catalysts could be used for catalytic processes. The homogeneous catalysts have a series of properties that make them suitable catalysts for biodiesel production. But the separation of them is usually difficult. In large-scale plants, the handling and assembling of them seem to be difficult (Salimi and Hosseini, 2019; Gardy et al., 2019).

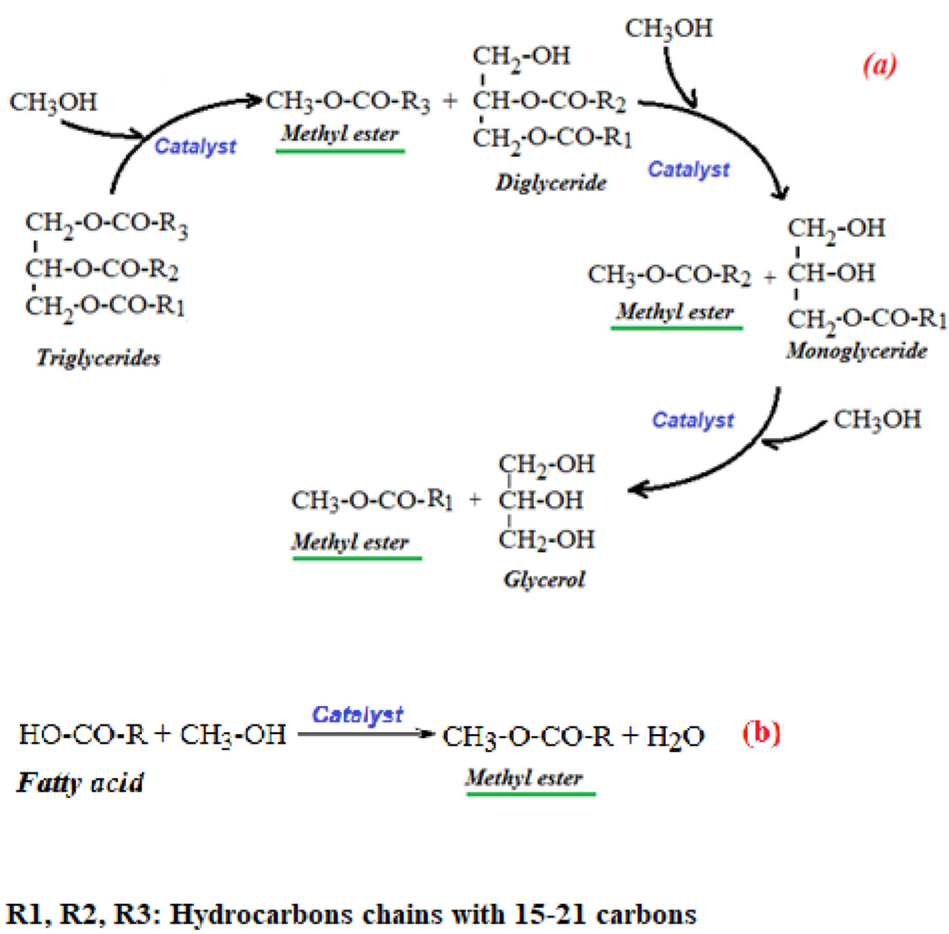

Fig. 1 Transesterification reactions of Glycerides with methanol to get methyl esters (a); Esterification of fatty acids to produce biodiesel (methyl ester) (b).

2.1. Homogeneous catalysts in biodiesel production

The homogenous catalysts have been investigated for esterification, ester hydrolysis, and transesterification. The homogeneous catalysts are divided into acid and base catalysts. The usual alkali homogenous catalysts for biodiesel production are often NaOH, KOH, NaOCH3, and KOCH3. The studies indicated that the alkali catalysts could speed up the transesterification reaction of low free fatty acid (FFA) much more than acid catalysts, whereas, in the case of the oils containing high FFA or high water content, the homogenous acid catalysts are preferred (Banković-Ilić et al., 2017; Salimi and Hosseini, 2019).

Transesterification by alkali catalysts is the conventional route for biodiesel production from pure vegetable oils. In the biodiesel reaction, three moles of alcohol react with one mole of triglyceride to produce glycerol (1 mol) and fatty esters (3 mol). The optimum ratio of alcohol to triglyceride was 6:1to reach a biodiesel yield of 98 %. Some studies indicated that alkali metal methoxides (methoxide salts) are more active than alkali metal hydroxides for biodiesel production (Gardy et al., 2019; Felizardo et al., 2006; Marris, 2006). The yield of biodiesel is reduced and separation gets difficult when more than 0.5 wt% of FFA exists in the feedstocks due to soap formation. Also, for the feedstocks containing high water (more than 6 wt%), the yield of biodiesel production decreased, because of the sensitivity of the alkaline catalysts towards moisture and free fatty acids. The existence of water in feedstock decreases the yield of biodiesel and is needed to use more catalysts during the process. So, the reduction of the water in feedstock by pretreating FFA is needed for the transesterification reaction catalyzed by alkaline catalysts. Furthermore, the solubility of the catalyst makes it difficult to separate the catalyst from the products (Gardy et al., 2019; Zhang et al., 2014).

Besides, the acid catalysts used in the esterification process are HCl, H_2SO_4, H_3PO_4, organic sulfonic acids ($R\text{-}SO_3H$), and boron trifluoride (BF_3) (Samios et al., 2009; Moushoul et al., 2016). Acid catalysts can produce biodiesel from.

cheaper feedstocks, making the process more economical although it requires high temperature, takes place more slowly, and causes corrosion (reactors, pipes, vessels, etc) and other environmental issues; product separation and purification costs make it a less-attractive process. The transesterification reactions catalyzed by acids have less rate than the alkaline-catalyzed reactions (Koh and Mohd Ghazi, 2011). In these reactions, it is required expensive equipment to overcome the corrosion by acid (Gerpen, 2005; Lee, 2014; Lee et al., 2014). The disadvantages of homogeneous acid catalysts are that high concentration acidic catalysts are needed and the reaction is carried out at a high temperature (greater than100 °C). These conditions cause to form ether and partially burn the oil and finally reduce FAME yield (Gardy et al., 2019; Canakci and Van Gerpen, 2001). Furthermore, there are also some limitations such as separation of catalysts, sensitivity to water, FFAs in the feed and soap formation and needing to neutralize the catalyst.

2.2. Heterogeneous catalysts in biodiesel production

Heterogeneous catalysts have some excellent properties to be used as potential catalysts for biodiesel production. They are easily separated from the products and are noncorrosive. Also, they have an environmentally friendly nature and can be regenerated to reuse. Some suitable heterogeneous catalysts should be developed for biodiesel production from cheap feedstocks. Heterogeneous catalysts are prepared by various methods such as co-precipitation, sol–gel auto-combustion, vapour deposition, electrochemical methods, etc.

The heterogeneous catalysts are also divided into the base and acid catalysts.

2.2.1. Solid base-catalyzed transesterification

For the feedstock with low FFAs, the solid base catalysts show higher activities (Gardy et al., 2019; Lam and Lee, 2011; Wilson and Lee, 2012). Many solid base catalysts were applied in biodiesel production. Some alkali base catalysts include alkaline earth oxides, alkali metal-doped alkali earth oxides, alkaline earth oxides, hydrotalcite, alkali zeolites (Al-Jammal et al., 2016) and supported alkali metals (Gardy et al., 2019). Calcium oxide is the most common basic metal oxide that is used in biodiesel production. It has the advantages of heterogeneous catalysts and is cheap, drawing the.

attention for further investigations of CaO. In the microstructure form, it has a low surface area (Salimi and Hosseini, 2019; Gardy et al., 2019). In the next sections, some examples will mention the application of these catalysts in biodiesel production. The solid base catalysts exhibit some problems, especially in commercial applications such as slow reaction rate, dissolution of catalyst in the reaction medium, and catalyst leaching. The solubility of catalysts in methanol decreases when the basicity of the catalyst increases. Because of these problems, more investigation should be done to find cheap and active catalysts for transesterification reactions to produce biodiesel (Gardy et al., 2019).

2.2.2. Solid acid catalysts in biodiesel production

Compared to solid base catalysts, the solid acid catalysts exhibit low activity, needing higher reaction temperature and a longer time for transesterification reaction. However, they have high stability. The solid acid catalysts are promising for converting the feedstocks containing high FFAs and water (Gardy et al., 2019; Al-Jammal et al., 2016; Hara, 2009). In addition, it is stated that in the case of waste oils with free fatty acids of more than 2 wt%, an acid-catalyzed system or heterogeneous catalysis would be preferable (Brito et al., 2007). This advantage led to the development of a wide range of solid acid catalysts to produce biodiesel such as zeolites, clays, transition metal oxides, mixed metal oxides, sulfated oxides, supported acids, sulfonated carbon-based materials, and waste and cation exchange resin (Gardy et al., 2019; Brito et al., 2007; Prabu et al., 2019; Aziz et al., 2017; Elimbinzi et al., 2018; Gardy et al., 2018; Kurhade et al., 2019; Tan et al., 2019; Rahimzadeh et al., 2018; Bora et al., 2018; Liu et al., 2010). Brito et al. (Brito et al., 2007) reported the application of several Y-type zeolites with different Al_2O_3 content as a heterogeneous catalyst in biodiesel production from waste oil. They concluded that the optimal condition reaction was achieved with zeolite Y530 at 466 °C, a space–time of 12.35 min, and a methanol/used frying oil molar ratio of 6 and with zeolite Y756 at 476 °C and space–time of 21.99 min, and the same feed mixture ratio.

The accessibility of the reactant to acid sites (Brønsted and Lewis) initiates the transesterification and esterification reactions and the type of the catalyst determines which reaction proceeds. These types of catalysts are not suitable for use in esterification and transesterification reactions on an industrial scale because of low catalytic performance, sensitivity to water or water resistance, and loss of catalytic sites.

Furthermore, low surface area and porosity and the deactivation of the solid acid catalysts are drawbacks. To use these catalysts in the reaction, it is needed a high ratio of methanol to oil (M/O), along with a high reaction temperature and long process time, especially for biodiesel production on an industrial scale. There are some review papers about the application of solid catalysts in biodiesel production (Liu et al., 2010; Zabeti et al., 2009).

2.3. Esterification by enzymes

The enzymes, the biological catalysts, can handle the transesterification reaction of vegetable oils or animal fats. Lipase enzymes are the main enzymes for this purpose. The enzymes are used to convert the raw materials containing high FFAs into FAME. The Enzymes for the production of biodiesels have some advantages and disadvantages. The advantages of enzymes are that they catalyze the reaction under mild conditions. Also, they are applicable for feedstocks with high FFA content and no saponification occurs during purification and neutralization issues (Shahid and Jamal, 2011). The biodiesel production by the enzyme catalysts is expensive and the reaction needs a long time and the reuse of the catalysts is limited. The yield of biodiesel obtained from the enzymatic reaction is relatively low, making it less economical (Zuliani et al., 2018).

3. Nanocatalysts for biodiesel production

Recently, nanotechnology is used to prepare nanocatalysts for biodiesel production. Nanocatalysts are formed from nanoparticles with different shapes and morphologies with a cross-section of less than 100 nm (Polshettiwar and Varma, 2010). They stand at the boundary between heterogeneous and homogeneous catalysis since one can refer to pseudo-homogeneous catalysis, exhibiting the advantages of both heterogeneous and homogeneous catalysts in terms of activity, selectivity, efficiency, and reusability (Polshettiwar and Varma, 2010; Diercks et al., 2018; Yamamoto et al., 2009; Fukuda et al., 2001). The nanocatalysts do not have the limits of homogeneous and heterogeneous catalysts. Herein, nanocatalysts used for biodiesels are divided into both magnetic and nonmagnetic categories and the investigation of their advantages and disadvantages is accomplished.

The mechanisms of transesterification of oil to biodiesel over both acidic and basic nanocatalysts are presented in Fig. 2. A mechanism for transesterification of oil (triglycerides) over acid nanocatalysts is presented in Fig. 2a. In this mechanism, the nanocatalyst provides a positively charged acid site for oil to get adsorbed on the nanocatalyst. After the adsorption of triglycerides on the acid sites of the nanocatalyst, the reaction between the methanol and triglycerides is started. This mechanism is similar to what is shown in Fig. 1, just the reaction speed is high on the nanocatalyst and is done under mild conditions.

The methanol is adsorbed on sites of the basic nanocatalyst to produce methoxide anions and hydrogen cations during the transesterification reaction. Then, the methoxide anions are reacted with a triglyceride molecule (oil) to produce FAMEs or biodiesel. The mechanism of the transesterification reaction on basic sites of nanocatalyst is shown in Fig. 2b.

3.1. Nonmagneticnanocatalysts

The ability to regenerate and reuse the solid catalysts makes it possible to lower-cost production of biodiesel and opportunities to operate in a fixed bed reactor. The mass transfer resistance is a common problem in heterogeneous catalysts and takes a long time to proceed with the reaction with acceptable efficiency. These drawbacks limit the application of bulk solid catalysts for industrial applications. The attempt to produce the catalyst with a small particle size and high active surface reduces the mass transfer resistance and helps to increase the yield of biodiesel production (Akia et al., 2014; biofueljournal, n.d.). There was an indirect relationship between particle size and the active surface of the catalyst (Banković-Ilić et al., 2017). A solution to solve the problem of the mass transfer resistance in catalysts is to reduce the particle size in the nanoscale and the development of nanocatalysts. Nanocatalysts usually have a high specific surface area (greater than50 m2 g^{-1}). Nanocatalysts due to having a large surface area resulted in a large number of catalytic sites and therefore high activity and causes to be frequently used in biofuel production (Banković-Ilić et al., 2017). The common nanocatalysts, used in biodiesel production are metal oxides, sulfated oxides, hydrotalcite, zeolites, zirconia, etc (Amini et al., 2013; Han and Guan, 2009; Boz et al., 2009; Feyzi and Shahbazia, 2015; Faria et al., 2009; Tamilmagan et al., 2015). Molina produced biodiesel from olive oils using ZnO nanorods and found that the catalytic performance of the ZnO nanorods (yield 94.8 %) was slightly better than that of the conventional ZnO (yield 91.4 %) (Akia et al., 2014; biofueljournal, n.d.; Molina, 2013).

Madhuvilakku and Piraman produced biodiesel from palm oil by ZnO and TiO2-ZnO nanocatalysts. The insertion of Ti ions in the Zinc oxide lattice led to make the defects in the oxide structure and promotes catalytic activity (Amini et al., 2013; Madhuvilakku and Piraman, 2013).

Borah et al., (Borah et al., 2019) used Mesua ferrea oil for biodiesel production using Co/ZnO nanocatalyst. They reported the maximum biodiesel yield of 98.03 % at methanol/oil of 9 at 60 °C for 3 h with 2.5 wt% catalysts. Zhang et al. optimized the process of biodiesel production over NaAlO2/γ-Al2O3 nanocatalyst by response surface methodology (RSM) (Zhang et al., 2020). The maximum biodiesel yield of 97.65 % was achieved at the M/O of 20.79:1, 10.89 wt% catalysts at 64.72 °C. The yield dropped to 52.16 % after three cycles because of active site leaching.

Baskar et al. (Baskar et al., 2018) produced biodiesel from castor oil with high free fatty acid using Ni-doped ZnO nanocatalyst. The response surface methodology (RSM) predicted 95.20 % at M/O of 8, 11 % wt.% catalyst at 55 °C for 60 min. The catalyst was able to be reused for 3 cycles.

As stated before, in the production of biodiesel the base catalysts exhibit more activity than acid catalysts and are more suitable for the process. So, the basic catalysts are mostly reviewed. Nayebzadeh et al. (Nayebzadeh et al., 2019) reported

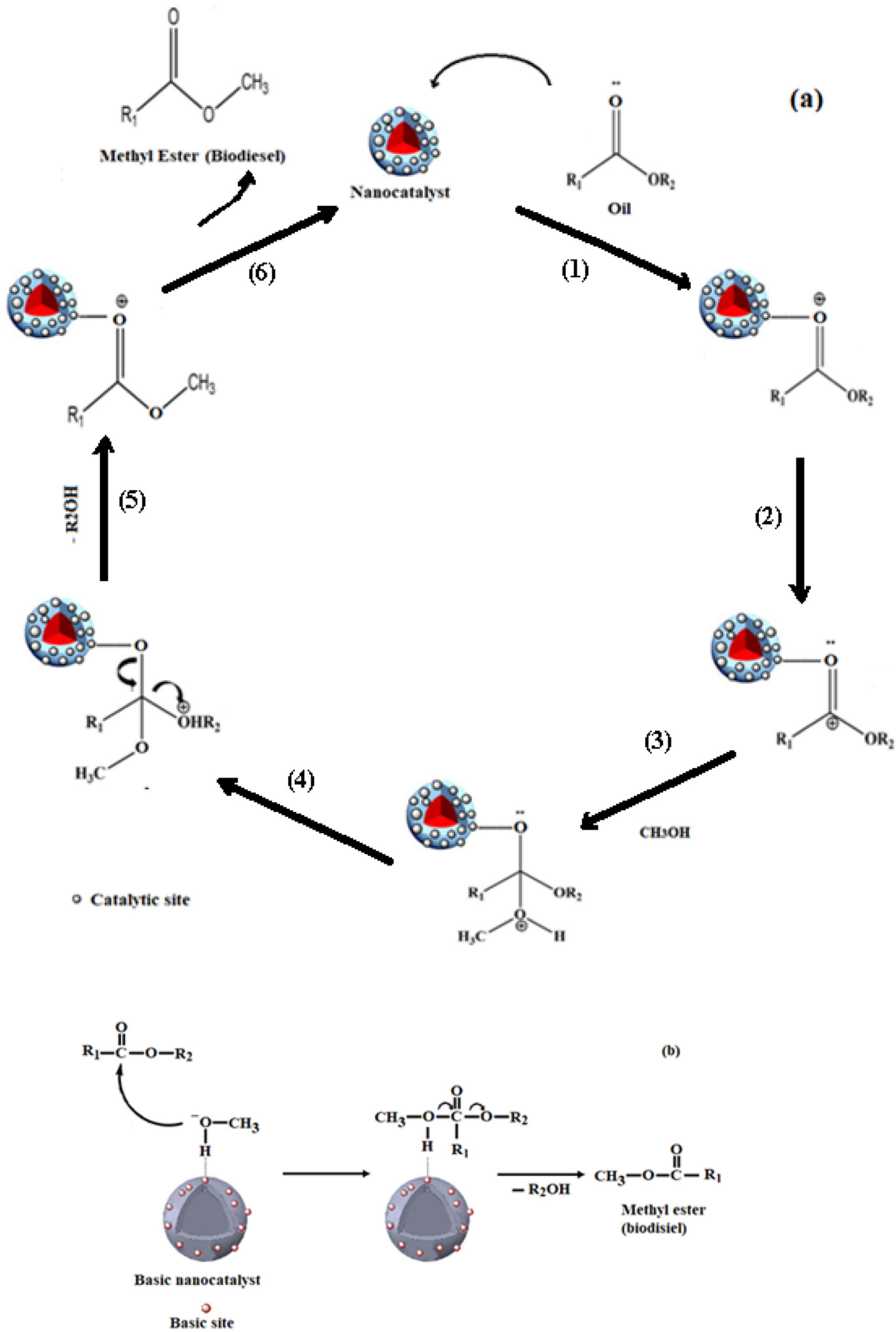

Fig. 2 The proposed mechanism for transesterification of oil over nanocatalysts. Acidic nanocatalysts (a) and basic nanocatalysts (b). R_1: carbon chain of fatty acid, R_2: alkyl group of alcohol.

KOH/Ca12Al14O33-C nanocatalyst for the production of biodiesel from canola oil. The nanocatalyst was a carbonated calcium aluminate and was synthesized by the microwave combustion method.

Ibrahim et al used Na2O/CNT catalyst for efficient biodiesel production from waste oil (Ibrahim et al., 2020). The catalyst was prepared by impregnation of Na2O on the CNTs and calcination at 500 °C for 3 h. The mechanism of the reaction was proposed. In this mechanism, Na + cations act as Lewis acids and oxygen as the Brønsted bases and enhance the activity of the catalyst. (Ibrahim et al., 2020). More than 97 % biodiesel yield resulted from the reaction under conditions of M/O of 20: 1, 3 wt% catalysts at 65 °C for 3 h.

Among the catalysts used for biodiesel production from waste oil, called first-generation biodiesel catalysts, the alkaline earth metal compounds, especially Ca-containing nanomaterials are promising catalysts for the transesterification of oils.

Mguni et al. (Mguni et al., 2012) reported the application of MgO/TiO_2 nanocatalyst for the transesterification of sunflower oil. They investigated three MgO loadings, i.e. 10, 20, 30 wt%, where the related conversions were 225 °C were 84, 91, and 95 %, respectively. The testing of these catalysts at 150 °C resulted in 15, 35, and 42 % conversion for 10, 20, and 30 wt% MgO, respectively. So, they concluded that at 225 °C, the catalyst contained 20 wt% MgO exhibited the highest activity.

Obadiah et al. (Obadiah et al., 2012) used Pongamia oil for the transesterification by calcined Mg-Al hydrotalcite and the process was optimized to get 90.8 % biodiesel yield.

The potassium bitartrate on zirconia support catalyzed the reaction of soybean oil and methanol to get 98.03 % biodiesel yield with M/O of 16 at 60 °C for 2 h (Qiu et al., 2011). Wen et al. (Wen et al., 2010) prepared KF/CaO nanocatalyst and used it for biodiesel production from Chinese tallow seed oil. The yield was 96.8 % for the M/O of 12 and 4 wt% of catalyst at 65 °C for 2.5 h. Deng et al. (Deng et al., 2011) reported the application of hydrotalcite with an Mg/Al molar ratio of 3:1 as a promising catalyst to obtain biodiesel from Jatropha oil (95.2 % yield) under ultrasonic conditions.

Kaur and Ali reported the biodiesel production from Karanja and Jatropha oils using Li/CaO nanocatalyst and got a 99 % yield for Karanja oil and Jatropha oil transesterifications after 1 h and 2 h, respectively (Kaur and Ali, 2011).

The production of 99 % biodiesel yield from soybean oil by nano CaO at room temperature was reported by Reddy et al. (Reddy et al., 2006). The nano CaO in different forms were studied and found that due to the higher surface area, small crystallite size and defects exhibit high yields of transesterification of soybean oil. Also, nano MgO has been studied for biodiesel synthesis from soybean oil by Wang and Yang at both supercritical and subcritical temperatures (Wang and Yang, 2007). They notices the catalyst activity was low under normal temperatures. At 60 °C, the methyl ester yield was only about 3 % after 3 h in the presence of 3 wt% of nano- MgO. The transesterification of triglycerides with methanol under more moderate conditions led to observing a 99.04 % yield in 12 min.

Metal-organic frameworks (MOFs) are high surface area and stable materials with adjustable tunnels that could be used as catalysts and nanocatalyst support in biodiesel production. Zhang et al. reported that the nickel salts of Keggin-type hetero-polyacids encapsulated into a metal–organic framework (UiO-66) hybrid nanocatalysts exhibited excellent activity and reusability for esterification of oleic acid or lauric acid with methanol over silicotungstic acid (Zhang et al., 2020; Zhang et al., 2019). Besides, they reported the synthesis of $Sn_{1.5}$PW/Cu-BTC by a simple impregnation method and its application as a novel nanocatalyst for producing biodiesel from oleic acid (OA) through esterification. The conversion of oleic acid was 87.7 % under optimum reaction conditions. The nanocatalyst was reused seven times, and after three uses, the OA conversion remained 80 % (Zhang et al., 2020).

Nano zeolites are another kind of nanocatalysts used in biodiesel production. Nanocrystalline zeolites have acid sites, shape selectivity, and high surface area, which are also used in biodiesel production on an industrial scale. De Vasconcellos et al. (de Vasconcellos et al., 2018) added (3-aminopropyl) trimethoxysilane (APTMS) to functionalize the nano zeolites with glutaraldehyde. They studied the activity of the enzyme–nano zeolite complexes in ethanolysis transesterification of microalgae oil to fatty acid ethyl esters (FAEEs) and demonstrate the role of the complex. The lipase-nano zeolite resulted in around 93 % FAEEs yield and kept its activity after five consecutive cycles.

Al-Ani et al. (Al-Ani et al., 2018) reported the application of mesoporous basic Faujasite-type catalysts in biodiesel production and promising catalytic results were obtained.

Potassium doped zeolite imidazolate framework used in biodiesel process from soybean oil by transesterification process (Saeedi et al., 2016). The conversion of 98 % resulted in a methanol/oil molar ratio of 10:1 for 3.5 h over the Na/ZIF-8 nanocatalyst. The nanocatalyst was recycled and reused three times. There are many papers about the application of nano zeolites in biodiesel productions (Kim et al., 2018; Al-Ani et al., 2019; Amalia et al., 2019).

Hydrotalcites are another kind of nanomaterials, used as nanocatalysts or catalyst support in biodiesel production (Chelladurai and Rajamanickam, 2014). The production of biodiesel in the presence of hydrotalcite can be carried out at ambient temperature. The application of nano-Zn-Mg-Al hydrotalcite as solid base catalysts for the production of biodiesel from neem oil through transesterification was proposed by Chelladurai and Rajamanickam (Chelladurai and Rajamanickam, 2014). Besides, the application of Mg/Al oxides derived from hydrotalcite was reported for transesterification of Jatropha oil with a 95.2 % yield of biodiesel by Dias et al. (Dias et al., 2012). The application of Mg-Al nano hydrotalcite for the methanolysis of neem oil was reported by Manivannan and Karthikeyan (Manivannan and Karthikeyan, 2013). In their study, the effect of the various reaction parameters was investigated and resulted that the reaction temperature played important role in the resulting yield of biodiesel. The maximum yield of 84 % was reported at a reaction temperature of 65 °C. More references about the application of hydrotalcite for biodiesel production are found in the literature (Gao et al., 2010; Sinha and Murugavelh, 2016; Prabu et al., 2019; Woodford et al., 2012).

3.2. Magnetic nanocatalysts

Recently, nanomagnetic catalysts were used for biodiesel production and are considered suitable for biodiesel production from cheap feedstocks (Mokhatr and El-Faramawy, 2021; Mokhatr et al., 2020). The magnetic properties can facilitate

Table 1 Details of reaction of biodiesel production on magnetic nanocatalysts.

Entry	Feed	Catalyst	conditions	Yield (%)	Ref.
1	Soybean oil	mixed iron/cadmium/ iron/tin oxide	Time: 1 h, T = 200 °C	84	(Mokhatr et al., 2020)
2	Date Palm seed oil	CaO/Fe_3O_4	T = 65 °C time = 300 min, M/O = 20, and 10 wt% of CaO/Fe_3O_4 catalyst loading).	69.7 %	(Alves et al., 2014)
3	Stillingia oil	$KF/CaO–Fe_3O_4$ (conc. 4 wt%)	T = 65 °C time = 180 min, M/O = 12	90 %	(Ali et al., 2017)
4	soybean oil	$Cs/Al/Fe_3O_4$	T = 58 °C, time = 120 min M/O = 14	94.8	(Hu et al., (2011))
5					
6	microalgae oil	Fe_3O_4/ZnMg(Al)O	T = 65 °C, time = 180 min M/O = 12	94	(Chen et al., 2018)
7	soybean oil	Guanidine-Functionalized Amphiphilic Silica Nanoparticles	T = 70 °C, time = 300 min M/O = 2.5	66.7 %	(Peng et al., 2020)
8	waste cooking oil	Lipase/amino silane modified Fe_3O_4	T = 40 °C, time = 48 h		(Kanimozhi and Perinbam, 2013)
10	Glyceryl trioleate (GT)	Catalyst I*	T = 100 °C, t = 20 h	88	(Wang et al., 2015)
	Oleic acid	Catalyst I	T = 70 °C, t = 4 h	100	
	Glyceryl trioleate (GT)	Catalyst II**	T = 100 °C, t = 20 h	100	
	Oleic acid	Catalyst II	T = 70 °C, t = 4 h	100	
11	Canola oil	CaO/NaY-Fe_3O_4	T = 65 °C, time = 5 h M/O = 8	95.37	(Hajitabar et al., 2017)
12	vegetable oil	$MgO/MgFe_2O_4$	T = 110 °C, time = 4 h M/O = 12	91.2	(Alaei et al., 2018)
13	Soybean oil	$Ni_{0.5}Zn_{0.5}Fe_2O_4$	T = 180 °C, time = 1 h M/O = 12	99.38	(Dantas et al., 2020)
14	Chicken oil	$CaO/CuFe_2O_4$	T = 70 °C, time = 4 h M/O = 15	94.52	(Seffati et al., 2019)
15	sunflower oil	$Ca/Fe_3O_4@SiO_2$	T = 65 °C, time = 5 h M/O = 15	97	(Feyzi and Norouzi, 2016)
16	waste cooking oil	*Citrus sinensis* peel ash (CSPA)@Fe_3O_4	T = 65 °C, time = 3 h M/O = 6	98	(Changmai et al., 2021)

* Sulfonic acid-functionalized Fe/Fe_3O_4.
** sulfamic acid-functionalized Fe/Fe_3O.

the separation of the catalyst from the reaction media, without needing centrifugal techniques and ultrafiltration. They maintained the catalytic activity for several cycles.

A wide range of magnetic nanomaterials have been recently synthesized and used for biodiesel production from cheap feedstocks, some of them reported below. Most of the magnetic nanocatalysts used in the process are in the form of a core/shell, where the Fe_3O_4 or other magnetic materials are the core. Table 1 presents the reaction details of some papers and some of them are described below.

Cadmium oxide and tin oxide nanocatalysts supported by magnetic material have been used in the esterification, transesterification, and hydrolysis reaction of soybean oil (Alves et al., 2014). In the esterification assisted by magnetic SnO, 84 % yield was achieved, at 200 °C after 1 h reaction. The catalyst was reused four times without loss in the activity. Mortadha A. Ali et al. reported the application of CaO-Fe_3O_4 as a nanomagnetic catalyst for biodiesel production from Date palm seed oil. The highest biodiesel yield was 69.7 % under the conditions of (65 °C reaction temperature, 300 min reaction time, 20 methanol/oil molar ratio, and 10 wt% of CaO/Fe_3O_4 catalyst loading) (Ali et al., 2017).

Liu et al. (Liu et al., 2010), reported the preparation of CaO/Fe_3O_4 nanocatalyst for methyl ester production and got 99 % and 95 % yield for the reaction using Ca $(OH)_2$ / Fe_3O_4 (1:7) after 4 h and 80 min, respectively.

Hu et al. (Hu et al., (2011)) reported the application of Stillingia oil for biodiesel production using KF/CaO-Fe_3O_4. The maximum activity resulted in 25 wt% KF/5 wt% Fe_3O_4; calcined at 600 °C for 3 h. Feyzi et al. (Feyzi et al., 2013) used Cs/Al/Fe_3O_4 nanocatalyst for biodiesel production from sunflower oil. The optimal catalyst showed high activity and a 94.8 % biodiesel yield resulted. The presented examples indicated that the nanocatalysts with a high surface area are more active in esterification than transesterification and hydrolysis reactions. In another paper, Tang et al (Tang et al., 2012) synthesized a magnetic Ca/Al/Fe3O4 composite by loading calcium aluminate onto Fe3O4 nanoparticles and reported its catalytic activity for preparing biodiesel with a biodiesel yield of 98.71 %. The composite kept its activity for 5 catalysis cycles.

Also, there is some paper about functionalized catalysts for biodiesel production. For example, Guanidine-functionalized Fe3O4 and Fe3O4@SiO2 nanoparticles as recyclable catalysts were applied in biodiesel production (Chen et al., 2018). Kanimozhi and Perinbam (Peng et al., 2020) reported the use of an extracellular lipase immobilized onto amino silane/Fe3O4 nanoparticles in biodiesel production from waste cooking oil. Wang et al. (Kanimozhi and Perinbam, 2013) studied glyceryl trioleate conversion to biodiesel over sulfamic and sulfonic silica-coated crystalline Fe/Fe3O4. They found that the sulfamic acid-functionalized nanocatalysts showed higher activity than the sulfonic acid-functionalized nanocatalysts. The above-mentioned examples could reveal the superiority of heterogeneous nanocatalysts compared to other traditional catalysts. The application of magnetic nanocatalysts due to their easy separation and reusability is important for the production of biodiesel.

Except for Fe_3O_4, some other magnetic materials have been used as a core of the core/shell catalysts. Some examples of these nanocatalysts are described below. Alaei and colleagues reported the application of magnetic MgO/MgFe2O4 nanocatalyst, synthesized via combustion method for biofuel production. The optimal conditions resulted in M/O of 12 at 110 °C and 4 wt% catalysts for 4 h, where a maximum biodiesel yield of 91.2 % was obtained (Alaei et al., 2018). Dantes et al. (Dantas et al., 2020) synthesized magnetic Ni0.5Zn0.5Fe2O4 and used it in the reactions of biodiesel production from soybean oil by both methyl and ethyl routes. The superior activity in the esterification reaction with conversions of 99.54 ± 0.1 6 % and 99.38 ± 0.18 % on the methyl and ethyl route, respectively. The nanocatalysts showed stability for 3 cycles. The maximum conversion for the transesterification reaction was 14 %. Seffati and co-workers (Seffati et al., 2019) reported biodiesel production by chicken fat with CaO/CuFe2O4 nanocatalyst with a yield of 94.52 % at the M/O of 15:1 at 70 °C and catalyst content of 3 % for 4 h. Some magnetic perovskites have also been studied in developing a magnetic catalyst for biodiesel production. For example, Salimi and Hosseini (Salimi and Hosseini, 2019) reported the magnetic ZnO/BiFeO3 nanocatalyst as a promising catalyst for biodiesel production from canola oil and found that under the optimum conditions, the biodiesel yields were 95.43 and 95.02 % in the first and second cycle, respectively. The optimum conditions were obtained at a catalyst dosage of 4 wt%, the molar ratio of methanol/canola oil of 15:1, and a reaction temperature of 65 °C.

Feyzi and Norouzi (Feyzi and Norouzi, 2016) reported the synthesis of a magnetic Ca/Fe3O4@SiO2 nanocatalyst using a combination of sol–gel and incipient wetness impregnation methods and used in the production of biodiesel. The nanocatalyst showed very effective activity at optimum conditions with a yield of biodiesel of 97 %.

4. Conclusion

Nowadays, fossil energies are running out and fossil energy resources should be replaced with safe and clean energies. Biofuels are a new source of energy that could be produced from biomass, waste foods, plants, etc. In the last years, the adequate choice of raw material and catalyst has been a critical point in determining the cost of biodiesel production in refineries and trying to minimize it. Depending on the situation, the homogeneous and bulk heterogeneous catalysts (acid and base) have some advantages and disadvantages. The esterification reactions catalyzed with alkali catalysts are faster than those acid-catalyzed. But in the case of a glyceride containing higher free fatty acid content and more water, the acid catalysts are preferred. Nowadays, nanocatalysts are usually used on a laboratory scale instead of bulk catalysts due to slow deactivation and the absence of mass transfer resistance. The nanocatalysts with high catalytic efficiency are often used under mild operating conditions which causes a reduction in energy consumption. Especially, magnetic nanocatalysts due to preventing nanoparticle loss and increasing their recovery rate during the separation process are more promising for the production of biodiesel by esterification and transesterification from waste oils. However, the safety of nanocatalysts is suspended to be used in biodiesel production. More investigations are needed to develop highly active and selective nanocatalysts, along with their economic feasibility for use in biodiesel production on an industrial scale.

Declaration of Competing Interest

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

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