

Production of renewable biodiesel using metal organic frameworks based materials as efficient heterogeneous catalysts

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ABSTRACT

Biodiesel has emerged as a versatile alternative to fossil-derived fuels which is a renewable and eco-friendly. The reactions via which biodiesel is synthesized from oil feedstocks are transesterification and esterification. These reactions are facilitated by certain catalysts which include both homogeneous and heterogeneous. Applications of homogeneous catalysts have been declining owing to certain limitations. The heterogeneous catalysts have been propounded as highly efficient catalysts for biodiesel production. However, the heterogeneous catalysts are also associated with a deficiency of active sites which adversely affect the catalytic performance. Recently, scientists have investigated various catalyst supports to enhance the catalytic activity among which metal organic frameworks (MOFs) and polyporous materials have gained the most attention. Several attractive features of MOFs such as high surface area, large porosity, tunable structures and functional groups, adjustable properties, uniformity in pore size, etc. are driving these materials as suitable catalysts for biodiesel synthesis. This review is focused mainly on the applications of MOFs-based catalysts and their catalytic performances in biodiesel synthesis. Different types of MOF catalysts, synthesis process, mechanisms, stability of the catalyst, and biodiesel properties are discussed herein. Moreover, other significant features of the synthesis of biodiesel such as production cost, economic viability, life cycle assessment, and applications of the machine learning techniques and reactors are highlighted and future perspectives are also discussed in this review. It can be emphasized from the study that MOFs could be developed as per the requirement for conversion of diverse qualities of feedstocks to biodiesel. Reactors such as microwave and ultrasound-assisted systems for the synthesis of both MOF catalyst and biodiesel are increasingly used in recent research to make the process cost-effective. Besides, applications of machine learning techniques in biodiesel research are found to be superior to conventional systems in modeling and optimization of the process.

1. Introduction

Human civilization, in general, is substantially reliant on natural resources for primary financial sections such as residential, transportation, industrial and commercial. The world has been going through rapid globalization as well as facing a swift increase in population density leading to the excessive utilization and ultimately dissipation of fossil fuels such as oil, coal, and gases. This results in environmental crises, worldwide climate change, adverse health effects due to

pollution, and increase in fuel prices which is most likely to affect the value of manufactured products and the economy of the nation (Banković-Ilić et al., 2017; Sadaf et al., 2018; Panahi et al., 2019; Kanakdande and Khobragade, 2020; Falowo et al., 2021). The most notable disadvantages of fossil fuels are that they are environmentally hostile, non-renewable, unsustainable, and noxious as they release harmful gases. These mineral fuels are not suitable for the environment and mankind in the long run (Barua et al., 2014). This is how the hunt for promising alternative fuel originates. Over the years, scientists have

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been exploring befitting alternatives to conventional fuels to overcome the constraints associated with the fuels (Bergmann et al., 2013). One of the promising substitutes for petro based fuel is a biofuel that can be produced from any bio-based low-cost feedstocks available around including plant materials and animal wastes. One of the fruitful biofuels which is gaining much popularity among scientists out of several alternatives is biodiesel and it is manufactured from biological sources such as oils or fats (Moser et al., 2009; Bergmann et al., 2013; Abdullah et al., 2017; Ramos et al., 2019). Biodiesel can be obtained from easily available sources like edible oils (commonly soybean oil), non-edible oils (jatropha, pongamia, rubber, etc), waste cooking oil (WCO), oil from algae, and animal fats (Mulyatun et al., 2022). Biodiesel is chemically manufactured by reacting triglycerides of vegetable oils or animal fats with short-chain alcohol forming mono-alkyl esters of long-chain fatty acids, also known as fatty acid alkyl esters. This method called transesterification reaction (Fig. 1) has been intensely studied. Biodiesel can also be produced by esterification of free fatty acids (FFAs) (Fig. 2) when the feedstock oil contains high FFAs (Deka and Basumatary, 2011; Abdullah et al., 2017; Sadaf et al., 2018). The reason behind its wide global attention is because of its attractive characteristics such as sustainability, renewability, biodegradability, non-toxicity, high flash point, high cetane numbers, sulfur-free nature, eco-friendly, and less carbon footprint (Basumatary, 2013; Mishra and Goswami, 2018; Sadaf et al., 2018; Nath et al., 2019).

Bioenergy crops such as edible vegetable oils are termed first-generation biodiesel feedstock. Food crops-based oils result in the conflict regarding the price between oil for food and that for fuel, and thereby price hikes in biodiesel may occur. To lessen the intrinsic higher price, emphasis on abundant and cost-effective raw materials is demanded (Basumatary et al., 2018). The high cost of biodiesel production is majorly associated with raw materials (Koh and Ghazi, 2011). One of the notable characteristics of employing biodiesel is the variety of non-edible oils. Non-edible oils such as *Madhuca indica*, *Azadirachta indica*, *Jatropha curcas*, *Pongamia pinnata*, *Ricinus communis*, *Hevea brasiliensis*, *Nicotiana tabacum*, field pennycress, etc. and various waste (used) cooking oils can be utilized as convenient and budget-friendly feedstocks (Koh and Ghazi, 2011; Basumatary, 2013; Aghbashlo and Demirbas, 2016; Gohain et al., 2017; Basumatary et al., 2018). Since the plants or vegetables consume the CO₂ released by the biodiesel-based vehicles, it contributes to carbon neutrality thereby reducing global warming (Ezebor et al., 2014). Biodiesel has physical and chemical properties similar to fossil-based conventional fuel for which it can be used directly in a diesel engine without any further modification (Nigam and Singh, 2011). Blended biodiesel with petroleum diesel in a different fraction is extensively used. Biodiesel can be considered much safer than conventional fuel from the standpoint of fire hazards and storage. Biodiesel has certain weak points. It is known that biodiesel has higher surface tension and viscosity which is recognized as a contributing aspect of high NO_x discharge. This can be eliminated by using short-chain alcohols during transesterification that produces monoester with less viscosity (Ferella et al., 2010; Huang et al., 2012). One of the trivial concerns of biodiesel is its vulnerability to degradation and

oxidation as the degree of conjugation increases in the double bond (Sazzad et al., 2016; Rodrigues et al., 2017). Implementation of biodiesel might face a struggle in complete approval of it as a promising substitute of conventional diesel if these issues remain unattended. One needs to adopt improved biological and chemical technologies to address the obstacles in the forthcoming days.

Catalyst is one of the requisite materials for the production of biodiesel. The notable characteristics for a catalyst to be efficacious are environmentally friendly, less consumption of reactant, corrosion-free nature, cost-effective, free of saponification and emulsion formation, and less alcohol to oil ratio (ATOR) requirement (Thangaraj et al., 2019). The catalyst can be categorized as homogeneous, heterogeneous, and biocatalysts. Biocatalysts can be used in the case of long-chain alcohol substrates such as butanol, iso-propanol, ethyl alcohol, etc. because of their decent unreactivity in the solvent. Even though these are highly specific and neat, the price associated with prohibits them from being used as suitable catalysts (Zabeti et al., 2009). Acid catalysts such as sulfuric acid, organic sulfonic acid, phosphoric and hydrochloric acid, etc. can be used if the glycerides have high FFAs content. Since they act at a much slower rate than that of base catalysts, these are less preferred (Nath et al., 2019). Homogeneous base catalysts such as KOH, NaOH, sodium hydride, potassium hydride, and alkoxides were used to yield high products at an industrial scale as they are abundant, cost-effective, and possess mild conditions (Al-Sakkari et al., 2018). These catalysts are considerably miscible in the reaction medium due to which saponification occurs (Fig. 3). This results in a large amount of catalyst consumption during the process and needs to be separated from the product which is laborious as well as expensive, and the biodiesel yield is significantly decreased due to soap formation (Michalska and Webster, 1974). These barriers associated with homogeneous acid or base catalysts make them unappealing elements (Freedman et al., 1984). These limitations offered scientists a new opportunity to search for a better solution. As a consequence, the heterogeneous solid base catalysts received the spotlight in recent times. The expansion of heterogeneous solid catalysts (HSC) has been achieving more recognition as they possess certain notable features that homogeneous catalysts do not have (Zabeti et al., 2009). HSC can be categorized into heterogeneous acid catalysts and heterogeneous base catalysts. Heterogeneous acid catalysts include sulfated metal oxides, heteropolyacid, acid ionic liquid, etc. Alkaline earth metal oxides such as MgO and CaO, basic anion exchange resins, hydrotalcite, basic ionic liquid, etc. are heterogeneous base catalysts (Zabeti et al., 2009; Chouhan and Sarma, 2011). These catalysts have minimum solubility in the reaction medium and are not consumed in the reaction, and hence these can be reused. In the process with oils that contain high FFA, initial neutralization is done with the help of an acid catalyst and then by the base catalyst in the second step leading to the simultaneous process of esterification and transesterification (Gandhi and Gogate, 2021). Since the solid catalysts do not cause saponification, a huge loss of water can be avoided from the purification process and ultimately results in a high product yield. HSC is less corrosive and environmentally and ecologically harmless (Degirmenbasi et al., 2015). HSC may have limitations to mass transfer, require high ATOR, a low

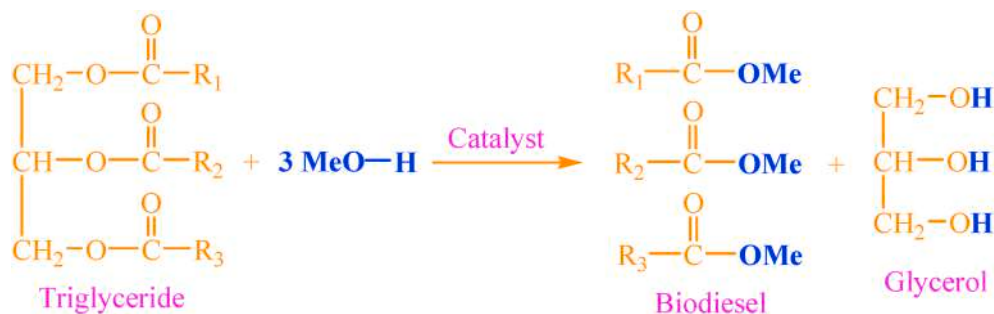


Fig. 1. Transesterification reaction (methanolysis) of triglyceride (oil/fat).



Fig. 2. Esterification reaction of FFAs using acid catalyst.

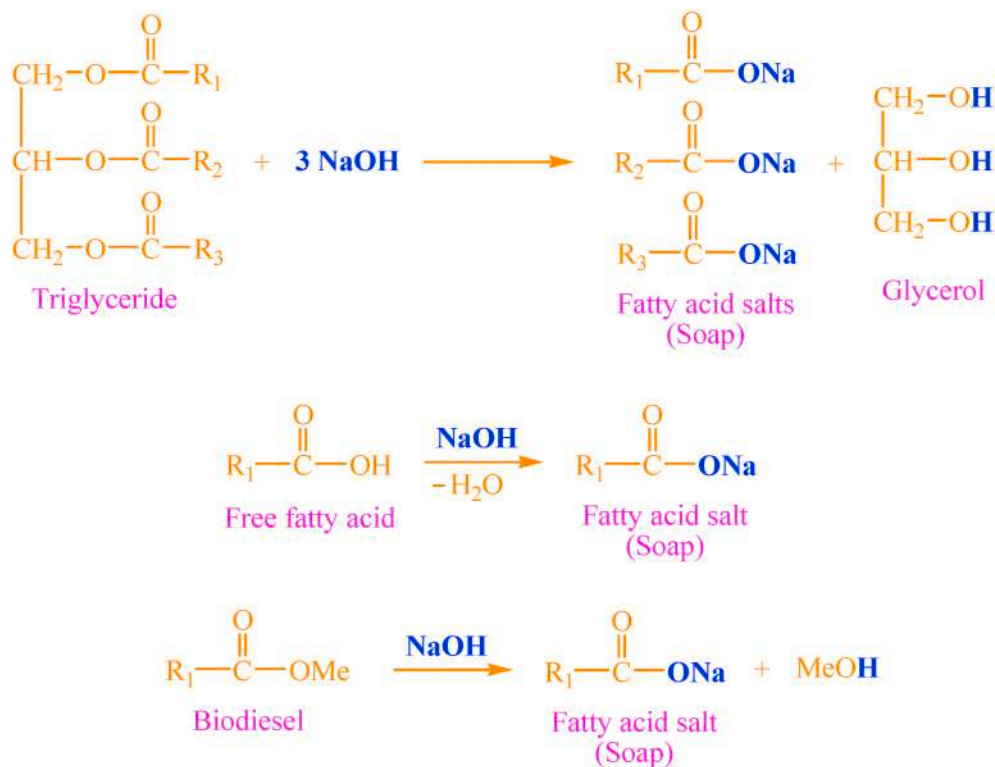


Fig. 3. Saponification reaction of triglyceride, FFAs and biodiesel.

active site for catalysis, and unable to carry out the reaction in mild conditions (Mbaraka and Shanks, 2006). To resolve these issues, certain diverse catalyst support such as alumina, silica, clay, zeolites, activated carbon, etc. can be used. Several studies on numerous catalyst support have been accomplished (Table 1) and some of these are Na/NaOH/ γ -Al₂O₃ (Taufiq-yap et al., 2011), KNO₃/Al₂O₃ (Vyas et al., 2009), KI/Al₂O₃ (Xie and Li, 2006), zeolite and metal catalysts (Babajide et al., 2012), calcined Mg–Al hydrotalcite (Gomes et al., 2011) and Li/CaO (Alonso et al., 2009). The purpose of using catalyst support is to increase the number of pores for the active site, increase the surface area and minimize the diffusion obstacle, and eventually decrease the reaction time (Shuit et al., 2013). Several studies have been reported using the heterogeneous catalyst as a favorable one for biodiesel production (Table 1). The catalysts reported by Liu et al. (2007), Liu et al. (2008a, 2008b), Vyas et al. (2009), Salinas et al. (2012), and Taufiq-yap et al. (2011), and many other chemical sources based catalysts (Table 1) have efficiency in the production of biodiesel. However, these are not considered the best for the process, not sustainable and non-biodegradable making them unsuitable for the environment, and flora and fauna. Therefore, the curiosity of researchers led to the exploration of other best-suited catalysts which are not only producing high yields but also cost-effective, eco-friendly, biodegradable, and sustainable. In recent times, scientists have been investigating the heterogeneous base catalysts derived from renewable natural resources, especially from agricultural wastes or biomass (Lam et al., 2010; Tobío-Pérez et al., 2021). Reusing of such materials constitutes no discarding problem and their applications to various operations provide

value addition to these wastes. Agro-waste is composed of organic compounds such as carbon and oxygen, and metals such as sodium, potassium, calcium, magnesium, metal oxides, carbonates, and other trace elements (Etim et al., 2020). Numerous wastes materials are being explored by several researchers (Table 1). *Musa paradisiaca* peel ash (Betiku and Ajala, 2014), cocoa pod husk (Rachmat et al., 2018), *Musa balbisiana* peel ash (Gohain et al., 2017), *Enterolobium cyclocarpum* (Falowo et al., 2021), rice husk ash (Chen et al., 2013), Moringa leaves ash (Aleman-Ramirez et al., 2021), *Musa acuminata* peel ash (Pathak et al., 2018), *Musa balbisiana* (underground stem) (Sarma et al., 2014), coconut husk ash (Husin et al., 2018), *Musa paradisiaca* (Basumatary et al., 2021a), *Sesamum indicum* (Nath et al., 2020), *Heteropanax fragrans* (Kessuru) (Basumatary et al., 2021c), sugarcane bagasse (Basumatary et al., 2021b), etc. are the notable precursor of heterogeneous base catalysts owning exceptional catalytic activity for biodiesel production.

Development and modification of porous materials have been progressing for various purposes over the few years and one of such examples is the metal organic frameworks (MOFs). The first catalytic application of MOF as heterogeneous catalyst in the cyanosilylation of aldehydes was reported in 1994, where Fujita et al. (1994) utilized Cd(NO₃)₂ and 4,4'-bpy to produce {[Cd(4,4'-bpy)₂]NO₃]₂}. The first hydrothermal synthesis of MOFs was done in 1995 by Yaghi and Li (1995) utilizing Cu(NO₃)₂·2.5H₂O, 4,4'-bpy, and 1,3,5-triazine. As shown in Fig. 4, MOFs find widespread applications in catalysis, gas storage, adsorption, biomedical field, sensors, magnetic material, solar energy conversion, etc. owing to their fascinating characteristics (Yap et al., 2017; Ajoyan et al., 2018; Manousi et al., 2018; Jiao et al., 2019; Cong

Table 1
Catalytic performance of different catalysts used in biodiesel synthesis.

Biodiesel feedstock/Alcohol	Catalyst	Surface area (m ² g ⁻¹)	Reaction conditions				Reference	
			Alcohol to oil ratio (ATOR)	Catalyst (wt %)	Temp (°C)	Time (h)		Product, Y or C (%)
Soybean oil/methanol	Nano-MgO	–	36:1	3	260	0.17	99.28 (C)	Wang and Yang (2007)
Soybean oil/methanol	SrO	1.05	12:1	3	65	0.5	95 (Y)	Liu et al. (2007)
Soybean oil/methanol	Calcium methoxide	19	1:1	2	65	2	98 (Y)	Liu et al. (2008b)
Waste cooking oil/methanol	Zinc stearate immobilized on silica gel	–	18:1	3	200	10	98 (Y)	Jacobson et al. (2008)
Palm oil/methanol	Na/NaOH/ γ -Al ₂ O ₃	–	15:1	3	60	3	99 (C)	Taufiq-yap et al. (2011)
Jatropha oil/methanol	KNO ₃ /Al ₂ O ₃	–	12:1	6	70	6	84 (C)	Vyas et al. (2009)
Soybean oil/methanol	KI/Al ₂ O ₃	–	15:1	2.5	Methanol reflux temp	8	96 (C)	Xie and Li (2006)
Sunflower oil/methanol	Zeolite FA/Na-X	320	6:1	3	65	8	83.53 (Y)	Babajide et al. (2012)
Soybean oil/methanol	MgAl hydroxalicates	–	9:1	2.5	60–65	4	97.1 (Y)	Gomes et al. (2011)
Soybean oil/methanol	CaO	0.56	12:1	8	65	1.5	95 (Y)	Liu et al. (2008a)
Canola oil/methanol	K/TiO ₂	2	54:1	6	55	6	–	Salinas et al. (2012)
Waste cooking oil/methanol	Solid acid	–	30:1	10	80	8	92 (Y)	Lou et al. (2008)
Jatropha oil/methanol	Mg–Al hydroxalcite	24.69	30:1	5	160	4	93.4 (Y)	Wang et al. (2015)
<i>Thevetia peruviana</i> oil/methanol	<i>Musa paradisiacal</i> (plantain) peels	–	0.3 (v/v),	2.8	55	1.25	94.97 (Y)	Betiku and Ajala (2014)
Waste cooking oil/methanol	Cocoa pod husk	–	6:1	1	60	1	85 (C)	Rachmat et al. (2018)
Waste cooking oil/methanol	<i>Musa balbisiana</i>	14.0	6:1	2	60	3	100 (C)	Gohain et al. (2017)
Waste cooking oil and <i>Calophyllum inophyllum</i> oil/methanol	Ba(OH) ₂	–	6:1	1.75	–	1 min	98.8 (Y)	Falowo et al. (2021)
Waste cooking oil and <i>Calophyllum inophyllum</i> oil/methanol	Calcined biomass waste	–	6:1	1.75	–	4 min	100 (Y)	Falowo et al. (2021)
Soybean oil/methanol	Rice husk ash	–	24:1	4	65	3	99.5 (C)	Chen et al. (2013)
Soybean oil/methanol	<i>Moringa oleifera</i>	–	6:1	6	65	2	86.7 (Y)	Aleman-Ramirez et al. (2021)
Soybean oil/methanol	<i>Musa acuminata</i> peel	1.4	6:1	0.7	32	4	98.95 (C)	Pathak et al. (2018)
Jatropha oil/methanol	<i>Musa balbisiana</i> stem	38.7	9:1	5	275	1	98 (Y)	Sarma et al. (2014)
Cerbera manghas oil/methanol	Coconut husk ash	–	6:1	10	60	3	88.6 (Y)	Husin et al. (2018)
Jatropha oil/methanol	<i>Musa paradisiaca</i> trunk	6.4	9:1	5	65	0.15	97.65 (Y)	Basumatary et al. (2021a)
Sunflower oil/methanol	<i>Sesamum indicum</i>	3.6	12:1	7	65	0.67	98.9 (Y)	Nath et al. (2020)
Jatropha oil/methanol	<i>Heteropanax fragrans</i>	27.50	12:1	7	65	1.08	97.75 (Y)	Basumatary et al. (2021c)
Jatropha oil/methanol	Waste sugarcane bagasse	7.66	9:1	10	65	4.75	92.84 (Y)	Basumatary et al. (2021b)

ATOR–Alcohol to oil ratio; wt–weight; Temp–temperature; C–conversion; Y–yield; h–hour.

et al., 2021; Ma et al., 2021). MOFs are a class of ultra-high porous crystalline hybrid materials constructed by self-assembling and forming coordination bonds between inorganic metal clusters and multi-topic organic ligands (Tan et al., 2021). MOFs have shown to have certain extraordinary and versatile properties owing to diverse structures such as pore size tunability for various purposes, enormous specific surface area, manageable composition, controllable environment, etc. (Chaemchuen et al., 2015; Mousavi et al., 2016). These supremacies have bestowed MOFs to be a prominent research objective, and the most notable one is being in heterogeneous catalysis (Pascanu et al., 2019). MOFs have emerged as an ideal substance to be used as catalyst support in biodiesel synthesis on account of mutable topological structures which enable pore accessibility for substrate molecules and high activity, and thus offer decent catalytic features (Gascon et al., 2013). The derivatives of MOFs are synthesized since the original MOF material has insufficient functional active sites and thus lacks activity. This can be addressed by modifying the structure in two possible ways which include (a) the impregnation and encapsulation (Fig. 5) of active components via intermolecular forces into the pores of MOFs, (b) the functionalization of certain groups (amino, carboxylic acid, sulfur) into the backbone of MOFs with active sites connected via covalent bonds (Cong et al., 2021). It is seen from Fig. 6 that different methods are employed for the synthesis of MOFs-based materials (Manousi et al., 2018; Cong

et al., 2021; Shomal et al., 2021). The commonly used methods are solvothermal and hydrothermal methods (Lee et al., 2013; Safaei et al., 2019; Cong et al., 2021). In solvothermal synthesis, the chemical reaction takes place in presence of a solvent at a temperature above its boiling point done inside a closed space known as an autoclave. Different types of solvents that can be used in this method can be alcohol, certain organic or inorganic solvents, and water where the synthesis is known as the hydrothermal method. This technique uses the self-assembly of products from soluble precursors. The solvothermal synthesis method does not require professional equipment and promotes crystal growth with high phase purity, and the whole process may take a longer time (several hours or days). The reaction may also be done in the absence or low amount of solvent via mechanochemical synthesis, however, requires high energy consumption (Lee et al., 2013; Safaei et al., 2019; Cong et al., 2021). To enhance the reaction rate, microwave-assisted solvothermal synthesis has been introduced. Microwave-assisted technology is energy efficient and produces high-quality nanosized crystals of MOFs in a very short time. This provides uniform and rapid heating of the molecules with less requirement of time (Lee et al., 2013; Safaei et al., 2019; Cong et al., 2021). The technique for the synthesis of high-quality nano MOFs is ultrasound-assisted technology. It is a green, energy, and economically efficient method that can provide high temperatures with uniform

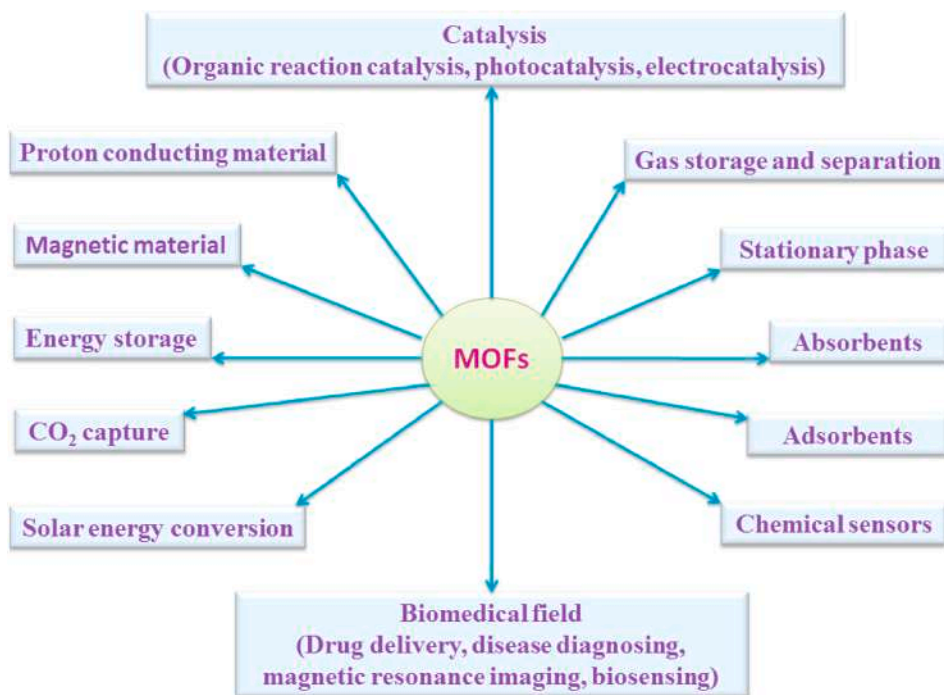


Fig. 4. Various applications of MOFs based materials.

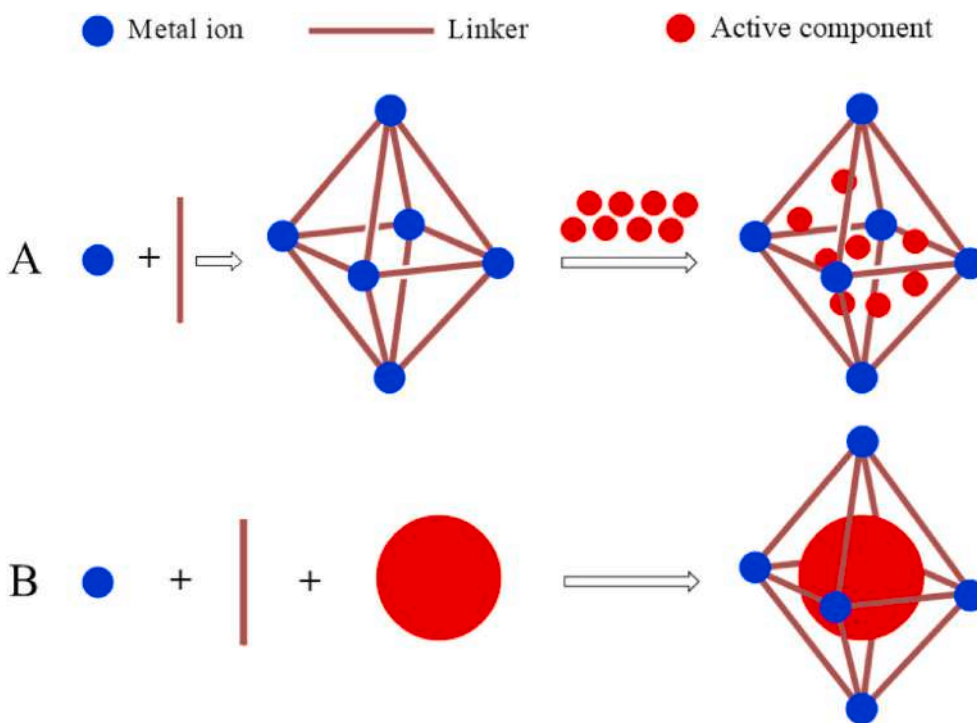


Fig. 5. Introduction of active components via intermolecular forces (A–Impregnation, B–encapsulation) into the pores of MOFs (Cong et al., 2021).

heating and pressure to complete the reaction in a short time. Electrochemical synthesis of MOFs can also be demonstrated for industrial-scale applications. In this method, instead of metal salts, the metal ions are used as a metal source to react with organic ligands and conduct salts present in the reaction medium. In comparison to the standard solvothermal method, this technique requires less reaction time and temperature (Lee et al., 2013; Safaei et al., 2019; Cong et al., 2021). MOFs can generally be categorized into four classes, viz. acidic

MOF catalyst, basic MOF catalyst, enzymatic MOF catalyst, and bifunctional MOF catalyst. Different MOF catalysts systems can be prepared after post-synthetic modifications of the structure of MOFs by encapsulating, immobilizing, and several chemical interactions. The current paper is aimed to review the catalytic behaviors of different structured MOFs in transesterification and esterification reactions for biodiesel synthesis reported so far. The information on characteristics of different types of MOFs in transesterification and esterification reaction,

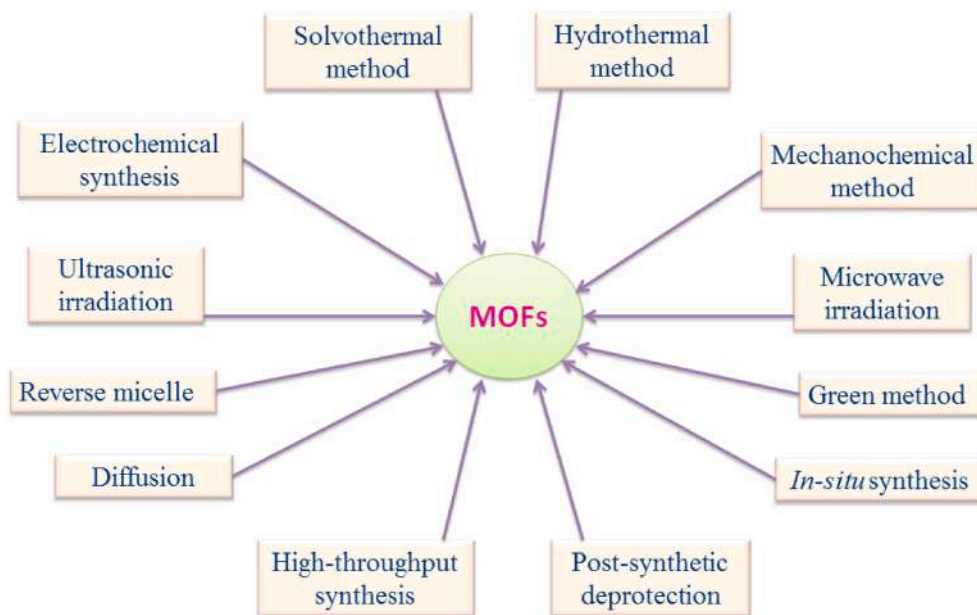


Fig. 6. Synthesis methods of MOFs based materials.

catalyst preparation, certain parameters associated, and recyclability of the catalysts will be extensively and methodically studied in this paper. Moreover, other significant features of the synthesis of biodiesel such as production cost, economic viability, life cycle assessment, and applications of the machine learning techniques and reactors are also highlighted and discussed in this review.

The references for this review are chosen from the publications in the area by searching from the Google and Scopus database. The keywords used were biodiesel, metal organic frameworks, and catalyst. The papers were selected based on the proper design of the study and experimental output with more data. The year-wise number of paper publications of MOFs-based catalysts used in biodiesel synthesis as of January 2022 is shown in Table 2. Table 2 showed that no publication on MOF-based catalyzed biodiesel synthesis could be seen till 2012. To the best of our knowledge, the first-ever paper on this topic was published by Du et al. (2013) that reported 44.7% conversion of palmitic acid to biodiesel using acidic MOF. Table 2 showed a gradual increasing trend in the publication of MOF-assisted biodiesel synthesis that increased from 3 articles in 2017 to 23 in 2021. As of January 2022, a total of 5 articles have already been reported in 2022 and it is expected to increase in the coming days. Finally, a total of 68 publications mainly on MOFs-based catalyzed biodiesel synthesis are incorporated in this study including 4 numbers of review articles.

2. MOFs catalyzed biodiesel synthesis via esterification and transesterification processes

The biodiesel production techniques using MOF-supported catalysts adopted in the conversion of oil feedstock to functional biodiesel are transesterification and esterification reactions. The pathway showing the synthesis of biodiesel using MOF catalysts is represented in Fig. 7. Both the reactions are extensively used either in the laboratory or industrial arena. Plenty of problems associated with both homogeneous acid and base-catalyzed reaction processes can be alleviated by adopting MOF as a carrier for various groups with catalytic properties. MOF structures can control their acidic and basic properties by managing the pore size and changing the functionalities. Owing to the large surface area, MOFs provide strong interaction between the metal ions and organic ligands. Thus, the active sites are strongly attached within the porous structure of MOFs reducing the problem of leaching and enhancing the overall catalytic activity. MOF composites are promising support for bifunctional catalysts as they can provide sites for both the basic and acidic functionalized groups and undergo transesterification and esterification reactions simultaneously. In both of these reactions, MOF-based catalysts are utilized with a key purpose to enhance the rate of destruction of carbonyl groups present in the reactants. The elemental strategy for base-catalyzed transesterification reaction is the extraction of protons (H^+) from methanol and the carbonyl carbon of triglycerides

Table 2

Year wise paper publication of MOFs based catalysts used in biodiesel synthesis as of January 2022.

Year of publication	Research article (Number)				Review article (Number)	Total publication (Number)
	Acidic MOF	Basic MOF	Enzymatic MOF	Bifunctional MOF		
2022	–	3	2	–	–	5
2021	13	1	5	1	3	23
2020	8	1	2	1	1	13
2019	5	2	1	2	–	10
2018	2	1	4	–	–	7
2017	2	–	1	–	–	3
2016	1	–	–	–	–	1
2015	1	1	–	1	–	3
2014	1	1	–	–	–	2
2013	1	–	–	–	–	1
2012	–	–	–	–	–	–
Total	34	10	15	5	4	68

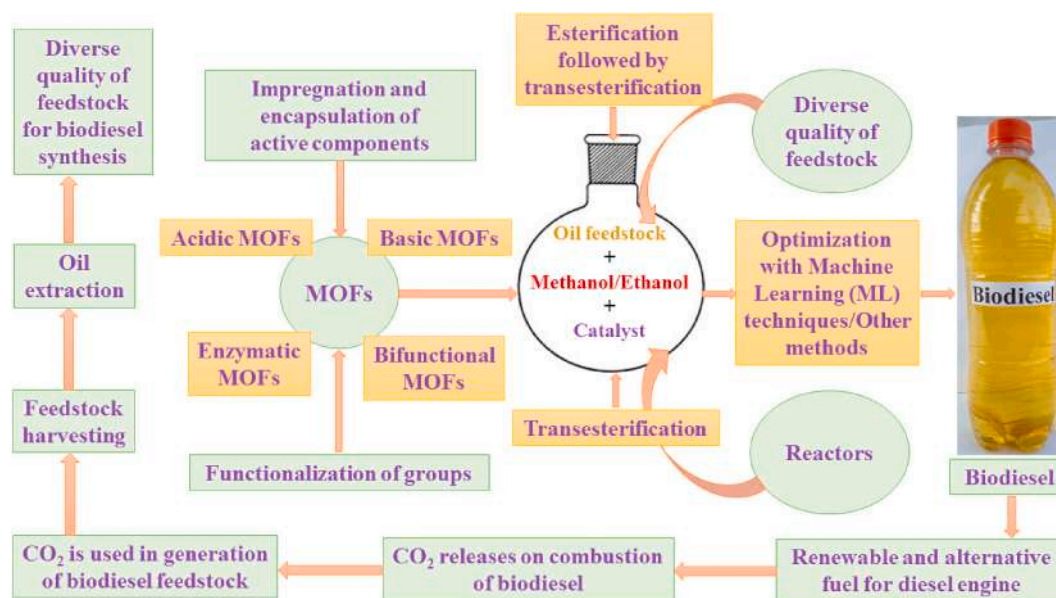


Fig. 7. Pathway showing the synthesis of biodiesel using MOF catalysts.

being attacked by methoxy anion. However, the way the catalysts approach may differ based on the active sites of the hybrid structures (Cong et al., 2021). Usually, the mechanism involves many steps of nucleophilic substitution reaction. For example, in a transesterification reaction using a ZIF-90-Gua catalyst (Xie and Wan, 2019c), the carbonyl group of triglyceride first interacts with the imine group of the catalyst and thereby forms the intermediate (Fig. 8). Then the nucleophilic attack of methanol on the intermediate occurs following the formation of a carbocation. Ultimately, the electron transfer and bond cleavage take place to achieve FAME (biodiesel).

The acid-catalyzed transesterification reaction proceeds with the combination of the carbonyl group of triglyceride and the protons provided by acidic MOFs. Then the reaction undergoes several steps finally forming the desired products, FAME and glycerol (Cong et al., 2021). The mechanism can be explained by taking the example of copper-based MOFs as a catalyst used in the transesterification of palm oil (Pangestu et al., 2019). The reaction consisting of Lewis acid catalyst such as CuBTC-MOF is usually assisted by several forces that include interface dipole-dipole, electron delocalization, and nucleophilic attack. The reaction proceeds via coordination of central Cu atom of CuBTC with methanol molecule as shown in Fig. 9. The central Cu atom also interacts with triglycerides induced by electron delocalization. These interactions provide better proximity to methanol and triglycerides for further reactions. The nucleophilic attack of the methoxy group on the electrophilic carbon atom of triglyceride occurs producing glycerol as a byproduct. Finally, the main product of biodiesel is obtained after being detached from the catalyst via electron delocalization at the oxygen atoms. Lunardi et al. (2021) conducted transesterification of palm oil using $Zn_3(BTC)_2$ catalyst and proposed a similar type of mechanism as shown in Fig. 9.

In the case of esterification reaction (Cirujano et al., 2015), the carbonyl of the carboxylic acid is protonated by the catalyst enhancing the electrophilicity of the carbonyl carbon. Afterward, the nucleophilic attack by the methanol group takes place followed by the formation of biodiesel and water (Cong et al., 2021). Fig. 10 (a) shows the esterification reaction of lauric acid using UiO-66 as a monofunctional acid catalyst and Fig. 10 (b) shows the reaction mechanism using UiO-66-NH₂ which acts as a bifunctional acid-base catalyst (Cirujano et al., 2015). The probable mechanism proposed by Zhang et al. (2020a) for the esterification using Zr-doped MOF-based nano-hybrid catalyst is similar to Fig. 10 (a). In the experiment conducted by AbdelSalam et al.

(2020), the microwave-assisted esterification reaction of oleic acid using Mg-MOF catalyst was observed to follow pseudo first order reaction. They reported the mechanism of this reaction that occurred with the initial step of diffusion of the reactants to the active site of the catalyst. Afterward, the reaction follows a similar pathway as shown in Fig. 10 (a). Lunardi et al. (2021) suggested a similar type of mechanism for esterification of vegetable oil with $Zn_3(BTC)_2$ catalyst as shown in Fig. 10 (a). The mechanism of esterification using $[(CH_2COOH)_2IM]HSO_4@H-UiO-66$ catalyst also followed the similar pathway (Ye et al., 2019).

2.1. Acidic MOF catalyzed biodiesel production

In order to avoid the environmental concerns associated with mineral acids in biodiesel synthesis, studies have led to alternative catalysts that are heterogeneous acid catalysts. These are not only stable but also exhibit excellent catalytic activity without needing for pretreatment process (Mo et al., 2008). Solid acid catalysts can facilitate the reaction with oils having a high acid value such as waste cooking oil, unlike solid base catalysts which are unsuitable to such oils. The application of low-quality and easily available oils with solid acid catalysts in the biodiesel synthesis process make them favorable for large-scale production. Besides catalyzing transesterification reaction, they can also assist the esterification reaction of FFA with alcohols (Ma et al., 2021). Nonetheless, some constraints associated with the solid acid catalyst such as leaching problem, low surface area, and small pore size need to be improved. Then, here comes the role of MOFs. MOFs, being highly stable and having adjustable functions as well as properties, can work as an appropriate support material for the functionalization of acidic groups (Hu et al., 2020a). Both the Brønsted acid and Lewis acid catalysts can be functionalized on MOF composites. Heteropoly acid (HPA) and polyoxometalate (POM) based catalysts have been gaining attention as Brønsted acid catalysts while some sulfated compounds are utilized as Lewis acid sites (Sani et al., 2014). Table 3 demonstrates the performances of different acidic MOF catalysts in biodiesel synthesis.

Wan et al. (2014) initiated to construct the ionic liquid, POM encapsulated within the cavities of MOF composite. Thereafter, they studied the catalytic performance of POM-based MOF for esterification to produce biodiesel. MOF composite was synthesized by using the one-pot hydrothermal method, where POM (12–14 Å) played the role of a bridge being inserted into the cages of the MIL-100 (MIL-Materials of

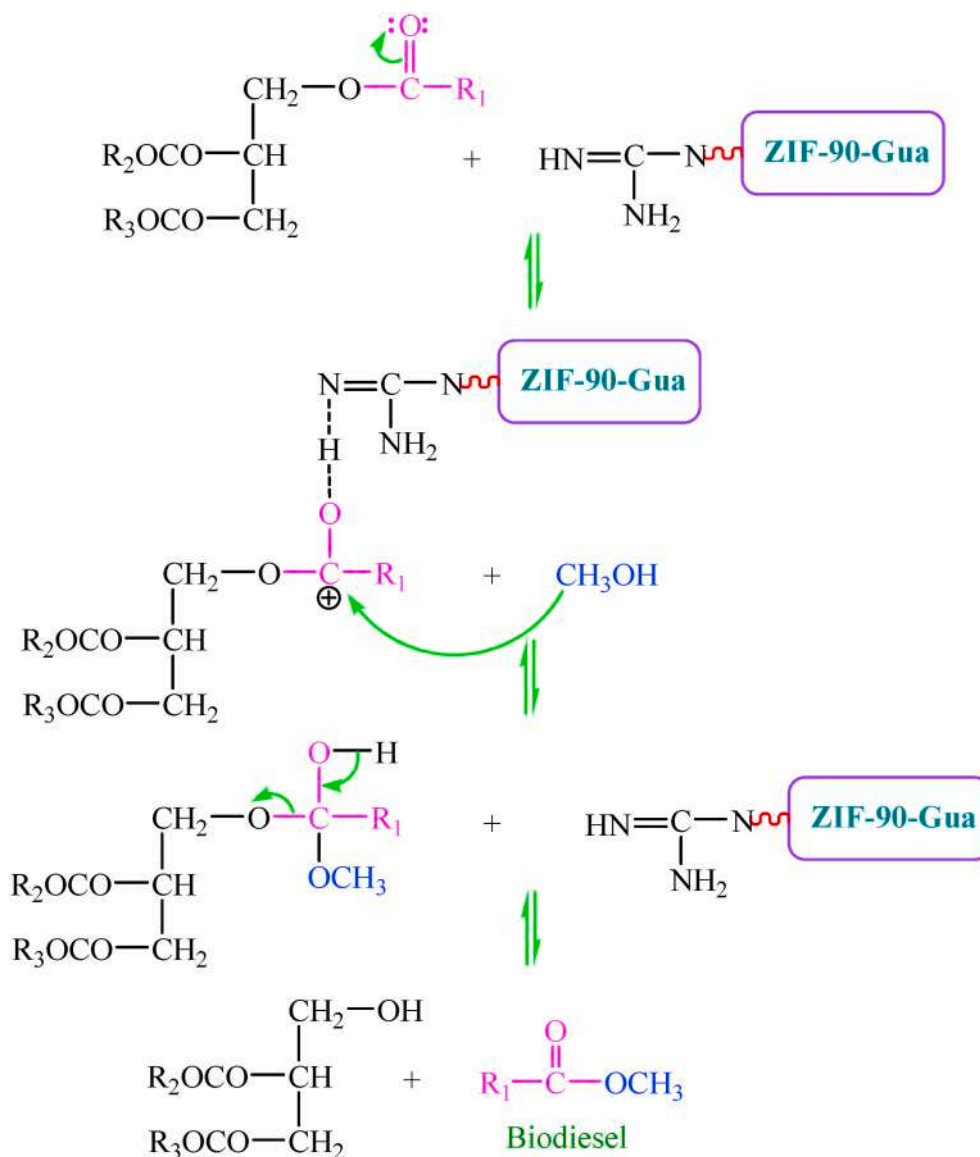


Fig. 8. Mechanism of ZIF-90-Gua based catalyzed transesterification reaction (Xie and Wan, 2019c).

Institut Lavoisier), thereby the heteropolyanion-based ionic liquid was encapsulated and produced. However, during the process of encapsulation, the interaction between the carrier and POM remarkably decreased the acidity of POM. Later, they improved POM-based MIL-100 by using the sulfonic acid group-functionalized ionic liquid to study the influence of heteropolyanion-based ionic liquid [SO₃H-(CH₂)₃-HIM]₃PW₁₂O₄₀. The resultant product, SO₃H-(CH₂)₃-HIM]₃PW₁₂O₄₀@MIL-100 was used for the esterification of oleic acid with ethanol. The catalytic activity was enhanced with the introduction of Brønsted acid sites by sulfonic acid groups which then worked together with initially present Lewis acid. This synthesis has been greatly accepted owing to several merits such as simple and eco-friendly process, presence of large active components, high stability and reusability, and easy separation. The XRD pattern of [SO₃H-(CH₂)₃-HIM]₃PW₁₂O₄₀@MIL-100 was found to be identical to that of HPW@MIL-100, indicating that the structure of MOF was preserved even after the introduction of ionic liquid. The HPW@MIL-100 showed a significant decrease in both surface area and pore volume which was 167 m²/g and 38 cm³/g, respectively. The loading amount of 0.83 mmol/g for [SO₃H-(CH₂)₃-HIM]₃PW₁₂O₄₀@MIL100 was obtained from elemental analysis data and the C, H, N content were found to be 25.42, 4.50 and 6.95%,

respectively. The analysis provided the maximum conversion using 15 wt% of catalyst amount, 11:1 ethanol to oleic acid molar ratio, 111 °C of reaction temperature, and 5 h of reaction time with 94.55% yield. After separation, the catalyst could be reused up to six times, resulting in considerable yield with no leaching of the active components. This study endowed the opportunity to unite the advantages of ionic liquid, POM, and MOF and thus produced a highly active and versatile heterogeneous catalyst for biodiesel production.

In a study by Hasan et al. (2015), sulfonic acid was used to functionalize MOFs to liquid-phase esterification of oleic acid and methanol. In their experiment, a highly porous MIL-101(Cr)-SO₃H was hydrothermally synthesized in a single step where they used sulfonic acid to functionalize the MOF. The characterization of the catalyst was done using various techniques such as XRD, FTIR, TGA, and nitrogen adsorption. In addition to liquid phase reaction, MIL-101(Cr)-SO₃H was also implemented in the vapor-phase reaction i.e. dehydration of 2-butanol to olefins. For the prepared catalyst MIL-101(Cr)-SO₃H, the surface area, pore volume, and acid density were found to be 1801 m²/g, 0.92 cm³/g, and 1.65 mmol/g, respectively. The esterification reaction was carried out under both conventional heating and microwave irradiation. A high product yield of 93% was obtained when certain

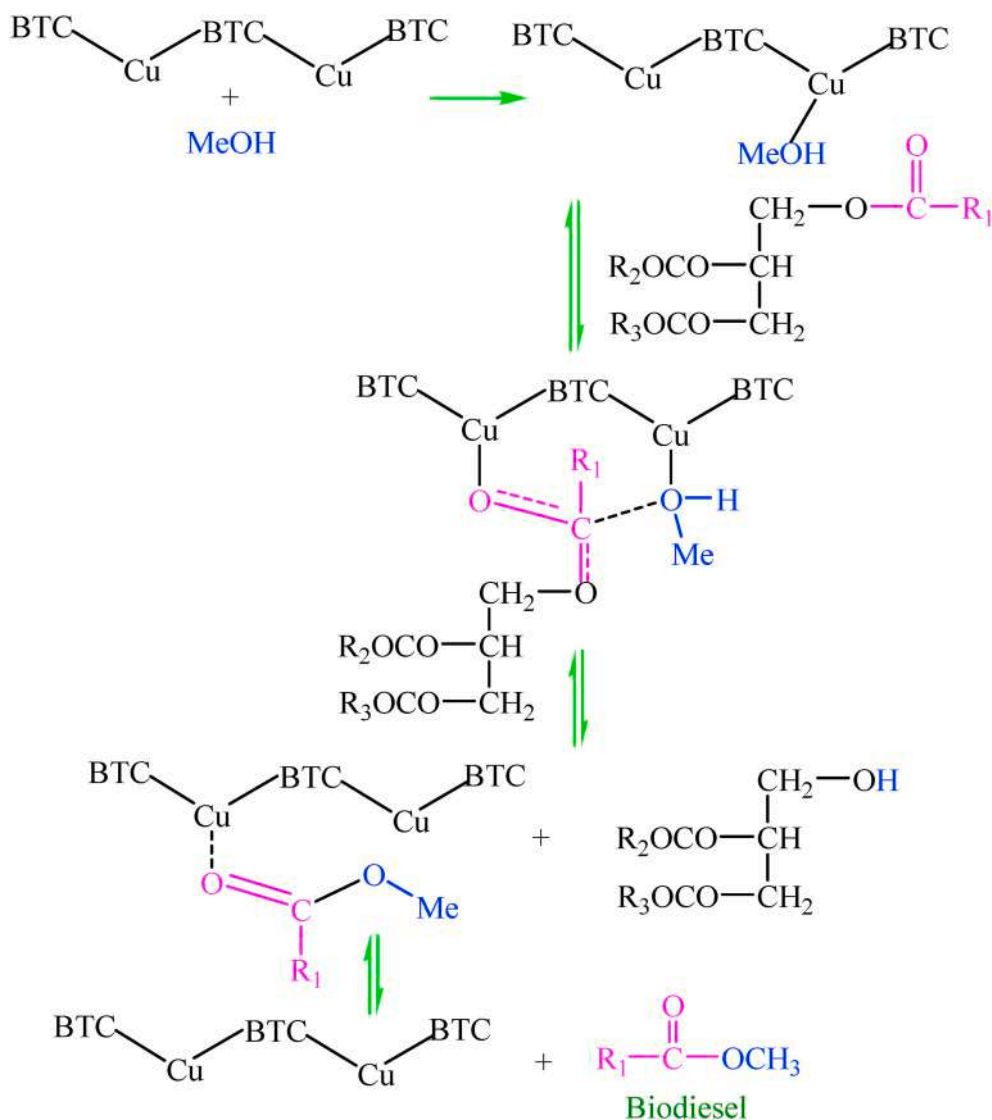


Fig. 9. Mechanism of CuBTC-MOF based catalyzed transesterification reaction (Pangestu et al., 2019).

optimum reaction conditions (ORCs) were applied. Under the action of microwave irradiation at 120 °C in 20 min, the faster reaction of esterification was reported. Moreover, when the vapor-phase catalytic reactions of 2-butanol to olefins using MIL-101(Cr)-SO₃H were compared with zeolite SAPO-34, the higher selectivities of the dehydrated products were obtained. The reusability and the application in both liquid- and vapor-phase catalytic reactions indicated the versatility of sulfonic acid-functionalized MOFs as a green and intriguing solid heterogeneous catalyst.

To address some issues of ionic liquids, scientists have employed solid materials as a support for the immobilization of ionic liquids to make them heterogenized. Among such experiments, a notable one is a research done by Wu et al. (2016) in which the magnetic MOFs are fabricated with the incorporation of ionic liquid to employ in biodiesel synthesis. For this purpose, the Brønsted ionic liquid 1, 4-butanediyl-3, 3'-bis-(3-sulfopropyl) imidazolium dihydrogensulfate (DAIL) was first prepared. The amino-functionalized MOFs labeled as NH₂-MIL-88B(Fe) were then prepared as support for ionic liquid. To enhance the performance of synthesized MOF, a magnetic composite Fe₃O₄@NH₂-MIL-88B(Fe) was prepared by attaching a magnetic Fe₃O₄ nanoparticle (NP) to it. The final catalyst was synthesized by incorporating Brønsted ionic liquid (DAIL) onto Fe₃O₄@NH₂-MIL-88B(Fe) via coordination of -NH₂ group of carrier and -SO₃H group of DAIL. The XRD analysis showed that the

crystalline structure of the NH₂-MIL-88B(Fe) remained unaffected even after hybridization with Fe₃O₄ and incorporation with DAIL. The FTIR analysis indicated a bit change in the spectrum of Fe₃O₄@NH₂-MIL-88B(Fe) after encapsulation of DAIL. The N₂ adsorption-desorption confirmed the microporous property of NH₂-MIL-88B(Fe) composite. After the immobilization of DAIL, the BET surface area of DAIL-Fe₃O₄@NH₂-MIL-88B(Fe) was observed to be decreased from 382.3 m²/g to 103.6 m²/g. The TGA analysis indicated that Fe₃O₄@NH₂-MIL-88B(Fe) was thermally less stable than DAIL-Fe₃O₄@NH₂-MIL-88B(Fe). The saturation magnetization value of DAIL-Fe₃O₄@NH₂-MIL-88B(Fe) reduced to 7.2 emu/g from the initial value of 12.5 emu/g, indicating a high loading amount of ionic liquid. In the external magnetic field provided by NdFeB magnet, the catalyst could be completely separated in a short time and exhibited superparamagnetic features. The esterification reaction of oleic acid and ethanol using the prepared catalyst was optimized by Box-Behnken response surface methodology (RSM) giving 93.2% conversion with high acidity. The ORCs were taken as 10.5:1 of ethanol to oleic acid molar ratio, 8.5 wt% of catalyst amount, 90 °C of reaction temperature, and 4.5 h of reaction time which were close to the predicted values. Moreover, even after being reused for six reaction cycles, the catalyst showed a slight loss in activity indicating good reusability character.

To investigate the catalytic activity of MOF-based catalyst in the

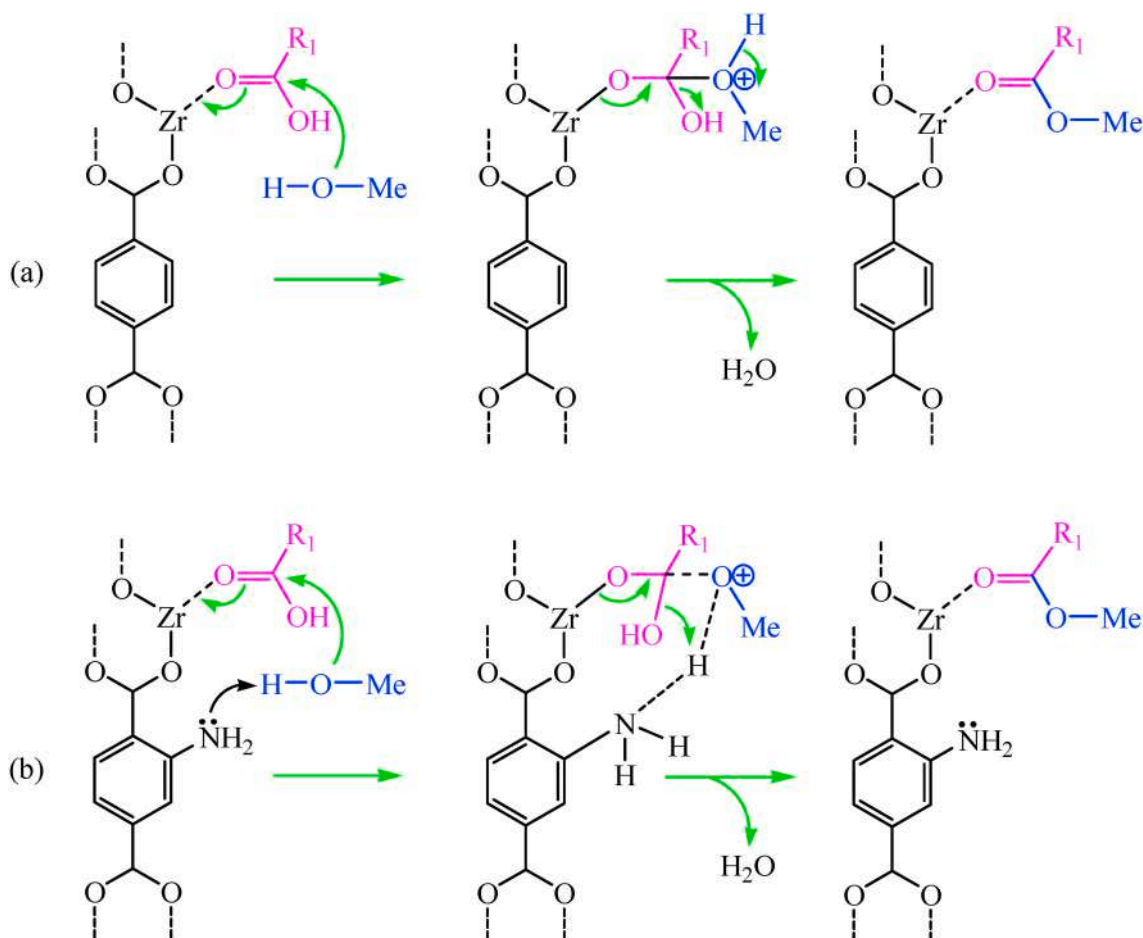


Fig. 10. Mechanism of esterification reaction of lauric acid catalyzed by (a) UiO-66 as monofunctional acid catalyst and (b) UiO-66-NH₂ as bifunctional acid-base catalyst (Cirujano et al., 2015).

esterification of oleic acid with methanol, Zhou and Chaemchuen (2017) had taken MOF materials viz. MOF-808, ZIF (Zeolite imidazolate framework)-8, and MIL-125. They compared the performance of these catalysts with traditional alumina (Al₂O₃) based catalyst as it possesses Lewis acid active site. At first, they synthesized ZIF-8-SV, and then MOF-808 was synthesized using a conventional solvothermal method followed by the synthesis of MIL-125 using a solvent mixture of DMF and methanol. Activation of the MOF materials was done by *in-situ* evacuation. The comparison between selected MOF-based composites and meso-alumina solid catalysts was evaluated under the same conditions. The catalytic activity on oleic acid esterification for non-catalyst, Al₂O₃, MOF-808, MIL-125, and ZIF-8 was studied taking 0.1 g of oleic acid, 10 mg of catalyst, and 1 ml of methanol at 130 °C. The result showed a higher percentage of yields up to 90% for all MOF catalysts in contrast to meso-alumina catalyst under the same reaction conditions. The reusability was checked for all MOF base catalysts and the catalytic activity remained significant up to the third experiment. When the weight loss of different catalysts was examined, the MOF-808, MIL-125 and meso alumina lost 3% of their weight after the third recycle process, whereas on each recycled reaction, ZIF-8 showed more than 10% weight loss. The study concluded that the high temperature needed for the functionalization of these catalysts is quite stringent in the aspect of industrial application.

Nikseresht et al. (2017) used microwave irradiation to accelerate the synthesis of Fe(III)-based MOF, viz. MIL-53 (Fe), which was suggested as a green and ecofriendly technique to boost the rate of chemical processes. The active catalyst was prepared by using heteropoly acid i.e. phosphotungstic acid (HPW), which was then immobilized in MIL-53

(Fe) that was initially synthesized using microwave irradiation. The resultant nanocomposite HPW@MIL-53 (Fe) was implemented as an active heterogeneous catalyst for esterification of oleic acid using ethanol and *n*-butanol to produce biodiesel. As the cavities of MOF composites were occupied by HPW, HPW@MIL-53 (Fe) showed lower weight loss as compared to bare MOF. The surface area of the catalyst was found to be 569 m²/g. They examined the effect of catalyst on esterification of oleic acid taking several amounts of catalyst (50–200 mg) by both alcohols (ethanol and *n*-butanol), and different reaction times (5–20 min) were employed as well. The ultrasonic irradiation output power was set as 100 W and 37 kHz frequency for best conversion. Out of various parameters used, the oil to ethanol molar ratio of 1:20 showed the worst performance of the catalyst. The maximum biodiesel yield of 96% was obtained by using 30% catalyst loading and 1:16 of oil to ethanol ratio in 15 min. Similarly, *n*-butanol showed maximum result at 30% catalyst and 1:16 of oil to butanol ratio yielding 98% of conversion. The result suggested that butanol produced a better product yield than ethanol. This might be explained based on the higher solubility of butanol in oleic acid than that of ethanol. Thus, the overall result showed successful conversion of oleic acid using MOF-based catalyst {HPW@MIL-53 (Fe)}.

Xie and Wan (2019d) studied the simultaneous transesterification and esterification of acidic vegetable oils employing MOFs modified with POM and sulfonated ionic liquids as a catalyst. In their experiment, Zr-based UiO-66-2COOH was utilized as MOF composite which was synthesized by refluxing H₄BTEC and ZrCl₄. UiO-66-2COOH was incorporated with Keggin type POM (HPW) via the *in-situ* synthesis method and then labeled as POM/UiO-66-2COOH. Afterward,

Table 3
Catalytic performance of different acidic MOFs catalysts.

Biodiesel feedstock/Alcohol	Catalyst	Catalyst preparation method	Biodiesel synthesis method	Surface area (m ² g ⁻¹)	Reaction conditions					Reference
					ATOR	Catalyst (wt %)	Temp (°C)	Time (h)	Product, Y or C (%)	
OA/ethanol	[SO ₃ H-(CH ₂) ₃ -HIM] ₃ PW ₁₂ O ₄₀ @MIL-100	Hydrothermal method	Esterification	555	11:1	15	111	5	94.55 (Y)	Wan et al. (2014)
OA/methanol	MIL-101(Cr)-SO ₃ H	Hydrothermal method	Esterification	1801	10:1	10	120	0.33	93 (Y)	Hasan et al. (2015)
OA/ethanol	DAIL-Fe ₃ O ₄ @NH ₂ -MIL-88B(Fe)	-	Esterification	103.6	10.5:1	8.5	90	4.5	93.2 (C)	Wu et al. (2016)
OA/methanol	MOF-808	Solvothermal method	Esterification	-	10:1	10	130	-	<90 (Y)	Zhou and Chaemchuen (2017)
OA/methanol	MIL-125	Solvothermal method	Esterification	-	10:1	10	130	-	<90 (Y)	Zhou and Chaemchuen (2017)
OA/methanol	ZIF-8	Solvothermal method	Esterification	-	10:1	10	130	-	90 (Y)	Zhou and Chaemchuen (2017)
OA/ethanol	PTA@MIL-53 (Fe)	Ultrasonic irradiation	Esterification	569	16:1	30	Ambient temp	0.25	96 (Y)	Nikseresht et al. (2017)
OA/n-butanol	PTA@MIL-53 (Fe)	Ultrasonic irradiation	Esterification	569	16:1	30	Ambient temp	0.25	98 (C)	Nikseresht et al. (2017)
SO/methanol	AILs/POM/Uio-66-2COOH	<i>In-situ</i> synthesis	Transesterification	8.63	35:1	10	110	6	95.8 (C)	Xie and Wan (2019d)
OA/methanol	AILs/POM/Uio-66-2COOH	<i>In-situ</i> synthesis	Esterification	8.63	-	20	Reflux temp	1.33	99.3 (C)	Xie and Wan (2019d)
PO/methanol	CuBTC-MOF	Solvothermal method	Transesterification	1085.72	10:1	0.08	60	4	91 (Y)	Pangestu et al. (2019)
OA/methanol	Sn _{1.5} PW/Cu-BTC-1	Impregnation method	Esterification	29.7	20:1	20	160	4	87.7 (Y)	Zhang et al. (2020c)
OA/methanol	Mg ₃ (BDC) ₃ (H ₂ O) ₂	Microwave irradiation	Microwave-assisted esterification	162	15:1	0.15	65	0.13	97 (Y)	AbdelSalam et al. (2020)
OA/methanol	MF-SO ₃ H	-	Esterification	6.18	10:1	8	70	2	95.86 (Y)	Liu et al. (2020)
OA/methanol	NiHSiW/Uio-66	Hydrothermal method	Esterification	692.3	18:1	6	160	3	86.7 (C)	Zhang et al. (2020b)
CIO/methanol	Cr-Tp MOF	Solvothermal method	Transesterification and Esterification	-	2:1	2.5	25	2	~93 (C)	Marso et al. (2020)
CIO/methanol	Co-Tp MOF	Hydrothermal method	Transesterification and Esterification	-	2:1	1	25	2	~93 (C)	Marso et al. (2020)
OA/methanol	UiO-66/SFN	Impregnation method	Esterification	4.93	8:1	8	70	2	96.2 (C)	Li et al. (2021a)
OA/methanol	PW-TiO ₂	Hydrothermal method	Esterification	9.4	20:1	15	160	4	90.5 (C)	Zhang et al. (2021c)
BA/butanol	UiO-66(1A:3C)	Solvothermal method	Esterification	761	2:1	1	Reflux temperature	24	92.2 (C)	Jrad et al. (2021)
BA/butanol	UiO-66(1A:3B)	Solvothermal method	Esterification	609	2:1	1	Reflux temperature	24	88.8 (C)	Jrad et al. (2021)
JCO/methanol	PSH/Uio-66-NO ₂	Impregnation method	Esterification	-	25:1	4	70	4	97.57 (C)	Dai et al. (2021)
PO/methanol	Zn ₃ (BTC) ₂	Solvothermal method	One-step transesterification and esterification	1176	6:1	1	65	4.5	89.89 (Y)	Lunardi et al. (2021)
OA/methanol	HPW@CoCeO	Solvothermal method	Esterification	20.5	30:1	10	60	4	67.2 (C)	Zhang et al. (2021d)
LA/methanol	Ag ₁ (NH ₄) ₂ PW ₁₂ O ₄₀ /UiO-66	Solvothermal method	Esterification	554.7	15:1	10	150	3	75.6 (C)	Zhang et al. (2020d)
OA/methanol	PMA/Fe-BTC	One-pot method	Esterification	108.3	16:1	10	160	3	72.3 (C)	Zhang et al. (2019a)
LA/methanol	HSiW-Uio-66	Hydrothermal method	Esterification	758.3	20:1	7	160	4	80.5 (C)	Zhang et al. (2019b)
OA/methanol	ZrSiW/Uio-66	Hydrothermal method	Esterification	249.4	20:1	24	150	4	98 (C)	Zhang et al. (2020a)
OA/methanol	ZrSiW/Fe-BTC	Hydrothermal method	Esterification	191.5	20:1	24	150	4	85.5 (C)	Zhang et al. (2020a)
OA/methanol	HSiW@ZrO ₂ -300	Hydrothermal method	Esterification	338	20:1	15	160	4	94 (C)	Zhang et al. (2021a)
OA/methanol	HPMo/Ni-MOF	Solvothermal method	Esterification	203.5	20:1	3	160	5	86.1 (C)	Zhang et al. (2021b)
SO/methanol	PW ₁₂ @Uio-66	Solvothermal method	Transesterification and esterification	1960	5.5:1	20	75	4	>90 (C)	Zhang et al. (2021f)
OA/methanol	HPMo/Cu-BTC	Hydrothermal method	Esterification	289	20:1	7	160	4	93.7 (C)	Zhang et al. (2021e)
PA/ethanol	IMFC-200	Hydrothermal reaction	Esterification	-	10:1	1	65	10	44.7 (C)	Du et al. (2013)
OA/methanol	UiO-G	-	Esterification	567.71	10:1	8	70	2	91.3 (C)	Li et al. (2021b)
JCO/methanol	MOF-5	-	Esterification and transesterification	-	36:1	0.75	145	9.59	88.3 (C)	Ben-Youssef et al. (2021)
WCO/methanol	MOF-5	-	Esterification and transesterification	-	36:1	0.75	145	12	90.8 (C)	

(continued on next page)

Table 3 (continued)

Biodiesel feedstock/Alcohol	Catalyst	Biodiesel synthesis method	Surface area (m ² g ⁻¹)	Reaction conditions		Time (h)	Product, Y or C (%)	Reference
				ATOR	Catalyst (wt %)			
OA/methanol	[(CH ₂ COOH) ₂ MIHSO ₄]/H ₂ UO-66	Esterification and transesterification	748	10.39:1	6.28	5	93.71(Y)	Ben-Youssef et al. (2021)
LA/methanol	H ₄ SiW/MIL-100(Fe)	Esterification	-	12:1	30	3	80.3 (C)	Ye et al. (2019)
Brythina mexicana/methanol	Co(II)-MOF	Transesterification	-	10:1	2.5	1.2	80 (C)	Zhang et al. (2020e) Pena-Rodriguez et al. (2018)
SO/methanol	AIL/HPMo/MIL-100(Fe)	Transesterification	-	30:1	9	6	92.3 (C)	Xie and Wan (2019b)
OA/methanol	AIL/HPMo/MIL-100(Fe)	Esterification	-	30:1	9	6	100 (C)	Xie and Wan (2019b)
SO/methanol	H ₆ PV ₃ MoW ₆ O ₄₀ /Fe ₃ O ₄ /ZIF-8	Transesterification	138.7	30:1	6	10	92.6 (C)	Xie et al. (2021)
FFA/methanol	H ₆ PV ₃ MoW ₆ O ₄₀ /Fe ₃ O ₄ /ZIF-8	Esterification	138.7	30:1	6	10	100 (C)	Xie et al. (2021)

ATOR-Alcohol to oil ratio; wt-weight; Temp-temperature; C-conversion; Y-yield; h-hour; ClO-Cataphyllum inophyllum oil; OA-Oleic acid; SO-Soybean oil; PO-Palm oil; LA-Lauric acid; PA-Palmitic acid; BA-Butyric acid.

POM/UiO-66-2COOH was immobilized by acidic ionic liquids [SO₃H-(CH₂)₃-HIM][HSO₄] reacting with heteropolyanion acids by anion exchange that formed AILs/POM/UiO-66-2COOH. By doing so, the difficulty in recovery associated with ionic liquids was eradicated as well as the MOFs could attain both Brønsted and Lewis acid sites enhancing their acidity and catalytic performances. The BET surface area and BJH pore volume of AILs/POM/UiO-66-2COOH were found as 8.63 m²/g and 0.04 cm³/g, while the mean pore size was obtained as 16.07 nm. The transesterification of soybean oil with methanol was performed using the prepared catalyst and after that, oleic acid was added purposely to the soybean oil for esterification of FFA present in the resultant oil feedstock. The transesterification achieved 95.8% conversion at 110 °C, 10 wt% of catalyst loading, and 35:1 MTOR in 6 h of reaction time. Moreover, the esterification of FFA obtained 99.3% conversion in the presence of 20 wt% FFA at the reflux temperature of methanol in 80 min of reaction time. The catalyst showed no remarkable decrease in oil conversion even after five consecutive cycles.

Pangestu et al. (2019) synthesized Lewis acid MOF as a catalyst for biodiesel synthesis from palm oil using methanol. In the study, they used Lewis acid metal, copper (Cu), and trimesic acid viz. benzene-1, 3, 5-tricarboxylic acid (BTC) to form a MOF composite (CuBTC-MOF). The MOF composite was synthesized using the solvothermal method with ethanol-water solvent, where the metal ions formed the coordination complex with three carboxylic acids present in BTC and its concomitant unit cell length was found to be 37.12 nm. The surface area and pore volume of CuBTC-MOF were determined to be 1085.72 m²/g and 1.68 cm³/g, respectively using BET isotherm. The average crystallite unit cell size for CuBTC was obtained as 37.12 nm by XRD analysis. At temperatures around 100–110 °C, CuBTC possessed a rod-like structure whereas the round-shape structure was obtained at a higher temperature. The thermal stability of CuBTC was observed in the range of 134–303 °C. The transesterification reaction was carried out using 5 g of palm oil, 50 ml of methanol, and 0.04 g of MOF at 60 °C for 4 h. The maximum yield of biodiesel at the aforementioned ORCs was found to be 91%. Moreover, the reusability of CuBTC-MOF was investigated which showed 86% yield of biodiesel after a single regeneration process indicating the good catalytic activity of the catalyst.

Heteropolyacids can be versatile as a strong Brønsted acid catalyst for esterification and transesterification reaction. However, owing to demerits of low surface area and high solubility in polar solvent make its use limited. To overcome the limitations, Zhang et al. (2020c) in their work used heteropolyacid on porous support materials i.e. MOFs for the efficiency of the catalyst. They prepared Keggin heteropoly nanocatalyst, Sn_{1.5}PW/Cu-BTC-1, consisting of Sn(II)-substituted 12-tungstophosphoric acid on a Cu-BTC matrix using encapsulation method to produce biodiesel. The particle size for Sn_{1.5}PW/Cu-BTC-1 hybrid was obtained in the range of 100–250 nm by SEM analysis. The surface area of Sn_{1.5}PW/Cu-BTC-1 decreased to 29.7 m²/g and the pore size increased to 7.11 nm. The ORCs were 1:20 M ratio of oleic acid to methanol, 0.2 g of catalyst, 160 °C of reaction temperature, and 4 h of reaction time resulting in high conversion of 87.7%. The reaction rate largely depends on the active sites of the catalyst. The activity of the catalyst remained significant providing 80% conversion even after the third cycle of reuse. Moreover, 60% yield was achieved after the 7th reaction cycle indicating the good reusability nature of the catalyst. The prepared nanocatalyst Sn_{1.5}PW/Cu-BTC-1 exhibited better stability as compared to other catalysts reported earlier before this study. The activation energy (E_a) of the reaction was found to be 38.3 kJ/mol.

AbdelSalam et al. (2020) made the use of microwave irradiation for biodiesel production using magnesium-based MOF (Mg-MOF), which was reported to be studied first by them. In this study, they constructed Mg functionalized MOF catalyst, {Mg₃(BDC)₃(H₂O)₂}; BDC-benzene-1, 4-dicarboxylic acid, which turned out to be less toxic and light-weighted. The synthesized catalyst was then employed for the esterification of oleic acid with methanol to produce biodiesel. From the BET isotherm, the surface area of the catalyst was found to be 162 m²/g.

The TEM analysis of the catalyst demonstrated that Mg-MOF is a transparent sheet with dimensions of ~150–250 nm and a thickness of less than 100 nm. In the absence of Mg-MOF catalyst, under microwave irradiation process at 10:1 MTOR for 10 min, a negligible conversion was obtained. The ORCs for the maximum yield of 97% were found to be 1:15 M ratio of oleic acid and methanol, and 0.15 wt% of catalyst at 65 °C in 8 min. The reaction followed pseudo-first order. The catalyst efficiency and the conversion remained constant till the fifth cycle of reaction.

Liu et al. (2020) demonstrated the study of concentrated sulfuric acid as an anchor of sulfonic acid (-SO₃H) to synthesize acid catalyst for the esterification of oleic acid with methanol. In their experiment, MIL-100 (Fe) was taken as a substrate which was functionalized with the help of dilute sulfonic acid to produce a clean and highly stable sulfonated catalyst, MF-SO₃H. The catalytic activity was found to be directly related to sulfuric acid concentration. According to the Hammett method, the acid strength of MF-SO₃H was found to be $3.3 < H_{\text{a}} < 4.8$. The pore volume and specific surface area were obtained as 0.015 cm³/g and 6.18 cm²/g, respectively. It was perceived that the structure of the MIL-100(Fe) was conserved by MF-SO₃H, the resultant product being stable up to 300 °C. The study showed high acid sites content at 70 °C that is both Lewis and Brønsted acid sites. The optimum conditions for catalyst preparation were found as 0.9 mol/L sulfuric acid concentration, 160 °C of sulfonation temperature, and 10 h sulfonation time. However, the esterification was completed in 2 h at 70 °C with a catalyst amount of 8 wt%, and methanol to oleic acid ratio (MTOAR) of 10:1. The maximum yield was found to be 95.86%. The conversion decreased on the reusability of the catalyst. Nonetheless, 88.50% of yield at the fifth cycle indicated the good reusability feature of the catalyst.

Zhang et al. (2020b) studied the catalytic properties of Ni-salts of Keggin-type heteropolyacid on Zr(IV)-based MOFs (UiO-66) for esterification of oleic acid. The hybrid nanocatalyst (NiHSiW/UiO-66) was prepared by encapsulating Ni-salts of Keggin-type heteropolyacids into Zr-based UiO-66 via ion exchange followed by a one-pot hydrothermal method. The high specific surface area and average pore size were found to be 692.3 m²/g and 4.40 nm respectively from N₂ adsorption-desorption analysis. The reaction was performed at ORCs of 18:1 MTOR and 180 mg of catalyst at 160 °C in 3 h, where 86.7% conversion was obtained. The catalytic efficiency was retained up to eight reaction cycles showing 50% conversion indicating its stability for biodiesel production. A kinetic study of the reaction showed pseudo first order kinetics with Ea of 69.2 kJ/mol.

Marso et al. (2020) investigated heterogeneous catalyst containing a Lewis metal ion combined with MOFs for esterification reaction. They employed chromium (III) terephthalate (Cr-Tp) and cobalt (II) terephthalate (Co-Tp) MOFs as heterogeneous acid catalysts for soap-free esterification of *Calophyllum inophyllum* oil (CIO) with methanol before the transesterification. They synthesized Cr-Tp MOF and Co-Tp MOF via the solvothermal and hydrothermal methods, respectively. Several successive catalytic cycles were used to perform esterification of oil at 2:1 MTOR, 25 °C of temperature, and 1 atm of pressure. The study indicated that only a small amount of catalyst (<2.5% of oil) and less amount of time was needed for the esterification reaction. The acid value of CIO significantly reduced from 56.91 to ~6.5 mg KOH g⁻¹ without causing saponification. After that CIO was subjected to the transesterification reaction. The ORCs for Cr-Tp MOF were found to be 2.5% of oil, 25 °C of temperature, and 2 h of reaction time. Similarly, for Co-Tp MOF, the conditions were 1.0% of oil, 25 °C, and 2 h. The percentage conversion of biodiesel from CIO was found to be ~93%. The reusability study showed that the catalytic activity remained significant even after the 10th cycle of reuse.

Li et al. (2021a) selected ammonium sulfate and UiO-66 to study the catalytic performance as an effective acid catalyst for biodiesel synthesis. UiO-66 usually consists of a secondary building unit of Zr₆O₄(OH)₄ which is 12-coordinated to terephthalic acid. In this experiment, UiO-66 was prepared by using 0.72 g of terephthalic acid, 50 ml of N,

N-dimethyl formamide, and 1.03 g of zirconium tetrachloride. The desired heterogeneous catalyst (UiO-66/S-P) was prepared using UiO-66 and (NH₄)₂SO₄ via the impregnation method. Further, the obtained catalyst was calcined in air and nitrogen atmosphere separately at 500 °C for 2 h. The resultant catalyst calcined under two different atmospheres were then named UiO-66/SFA, and UiO-66/SFN, respectively. UiO-66/SFN was again calcined in a nitrogen atmosphere under the same condition and named UiO-66/SSN. The esterification of oleic acid with methanol was then studied employing UiO-66/SFN as catalyst under the reaction parameters of 8 wt% of catalyst amount, 8:1 of MTOAR, 70 °C of temperature, and 2 h of reaction time producing 96.2% conversion. When the reusability was studied, the catalytic activity of UiO-66/SFN decreased from 96.2% to 57.12% in the 5th run.

Zhang et al. (2021c) conducted the esterification of oleic acid using heteropoly acid with strong Brønsted acid and a unique Keggin-type structure. Its low surface area and high solubility were overcome by attaching it to MOFs. In this study, MIL-125(Ti) MOF-derived nanoporous TiO₂-heteropoly acid (PW-TiO₂) was synthesized by the hydrothermal method. From the N₂ physisorption experiment, the surface area was found to be 9.4 m²/g. Similarly, the amount of acidity of the synthesized PW-TiO₂ composite was examined using temperature-programmed desorption of NH₃ (NH₃-TPD) which was found to be 2.7 mmol/g. The investigation revealed that the highest conversion of 90.5% was achieved under the ORCs of oleic acid/methanol ratio of 1:20, catalyst dosage of 0.15 g, 160 °C of temperature, and 4 h of reaction time. The reusability experiment provided more than 70% conversion up to the sixth cycle. The catalyst composite was further used for the esterification of *Euphorbia lathyris* oil with methanol and provided 73.7% conversion in 4 h indicating its ability to act as a promising heterogeneous catalyst for biodiesel synthesis.

In a study, Jrad et al. (2021) utilized the isostructural mixed organic linkers on MOF structure as a catalyst for the synthesis of biodiesel. They synthesized greatly defected and functionalized MOF first producing three single linker MOF viz. UiO-66, UiO-66(COOH)₂, and UiO-66(OH)₂ via the solvothermal method. Furthermore, the MTV approach was utilized to synthesize six other MOFs of UiO-66(COOH)₂ and UiO-66(OH)₂ integrating terephthalic acid (A) and 1, 2, 4, 5-benzene tetracarboxylic acid (B), and terephthalic acid with 2, 5-dihydroxy terephthalic acid (C), respectively using three varying ratios being 3:1, 1:1, and 1:3. The preparations of nine different MOFs with conditions are shown in Fig. 11. The surface area and pore volume of single linker UiO-66(COOH)₂ and UiO-66(OH)₂ were found to be 522 m²/g and 0.11 cm³/g, and 602 m²/g and 0.19 cm³/g, respectively. The number of defects for UiO-66(COOH)₂ and UiO-66(OH)₂ were obtained as 1.93 and 1.51, respectively. The esterification of butyric acid with butanol was studied using all the prepared catalysts. The ORCs taken for the reaction were 1 wt% of catalyst loading and 110 °C of temperature for 24 h. The most eminent conversion was obtained by MTV-UiO-66(OH)₂ and MTV-UiO-66(COOH)₂ i.e. UiO-66(1A:3C) and UiO-66(1A:3B) with 52% and 61% of functionalized linkers respectively. Their defects number were estimated to be 1.90 and 1.98 respectively. With BET surface area of 761 and 609 m²/g, UiO-66(1A:3C) and UiO-66(1A:3B) achieved the conversion of 92.2 and 88.8% respectively. Even after 4 successive cycles, UiO-66(1A:3C) preserved its catalytic activity and stability.

Dai et al. (2021) studied the combination of ionic liquids with MOF materials for the synthesis of biodiesel from *Jatropha curcas* oil (JCO). They synthesized a fresh ionic liquid with 1-methyl-imidazole, 1, 3-propyl sultone, and H₂SO₄. The prepared acidic ionic liquid was loaded into zirconium-based MOF viz. PSH/UiO-66, PSH/UiO-66-NO₂, and PSH/UiO-66-NH₂ by impregnation method. The catalytic activities of these catalysts were later compared with each other. The average conversions of JCO were found to be 66.21, 96.69, and 77.02% for catalysts PSH/UiO-66, PSH/UiO-66-NO₂, and PSH/UiO-66-NH₂ respectively at 70 °C, 3 wt% of catalyst, and 30:1 of MTOR in 5 h. The results indicated that the JCO conversion rate was better for PSH/UiO-66-NO₂ catalyst. The ORCs for PSH/UiO-66-NO₂ catalyst were

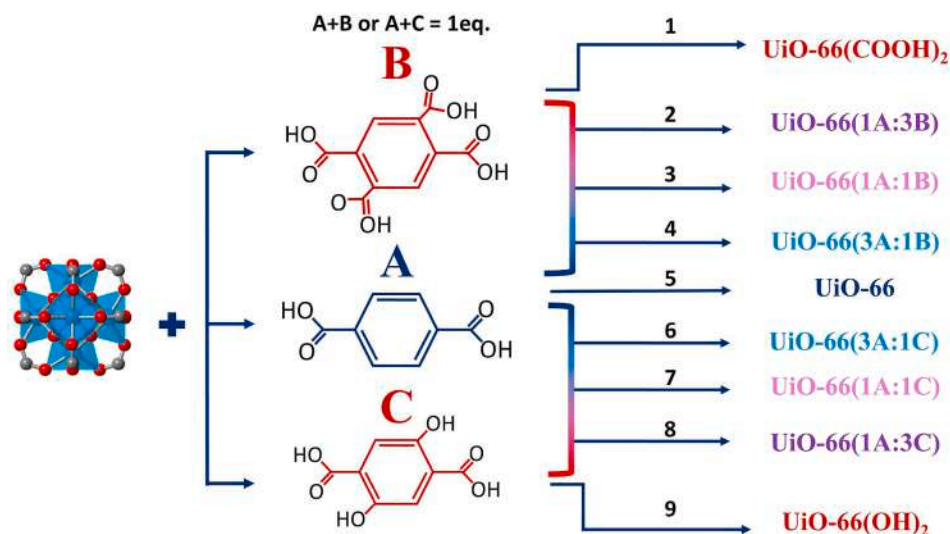


Fig. 11. Preparations of nine different MOF based catalysts. In the preparation mixture, 1 eq. is 1 M equivalent with respect to $ZrCl_4$. Reproduced from reference (Jrad et al., 2021) with permission of Elsevier, Copyright © 2021 (License no. 5263690039681).

investigated further by an orthogonal test. The ORCs were 70 °C of temperature, 25:1 of MTOR, and 4 wt% of catalyst in 4 h of reaction time with the conversion of 97.57%. After the third cycle, the conversion decreased to 77.14%. Thus from this experiment, it has been observed that PSH/UiO-66-NO₂ is a versatile acid catalyst to produce biodiesel from a low-grade oil with high catalytic activity and good reusability.

Lunardi et al. (2021) demonstrated the one-step transesterification and esterification of degummed palm oil for biodiesel synthesis using 3D Zn(II)-based carboxylate MOF known as Zn₃(BTC)₂. They first synthesized Zn₃(BTC)₂ by solvothermal method, where its 3D porous structure was constructed by the interaction between tritopic ligand H₃BTC and Zn²⁺ ions. During the process, H₃BTC ligands were fully deprotonated and a negatively charged BTC³⁻ species was formed resulting in a product with triclinic structure. The average size of the structure was determined to be 1.2 μm. BET surface area of 1175.81 m²/g, and pore volume of 0.81 cm³/g were reported. The analysis of variance (ANOVA) and the RSM-based Box-Behnken design (RSM-BBD) was applied for the optimization of reaction conditions. The maximum yield of 89.89% was obtained at 6:1 of MTOR, 1 wt% of catalyst, 65 °C, and a reaction time of 4.5 h. Moreover, it showed better turnover frequency in contrast to other MOF catalysts used for biodiesel synthesis. The efficiency of Zn₃(BTC)₂ catalyst came out to be stable even after three consecutive cycles without substantial metal leaching. This simultaneous conversion process can be economically viable and can boost the competence of biodiesel synthesis.

Zhang et al. (2021d) implemented a bimetallic MOF-derived catalyst loaded with phosphotungstic acid (HPW) for the esterification of oleic acid. Initially, bimetallic MOF-derived Co–CeO was synthesized via the solvothermal method and then HPW was impregnated onto porous cobalt cerium oxide by pyrolysis of CoCe-MOF to finally prepare HPW@CoCeO catalyst. The XRD analysis indicated a similar crystal structure for CoCe-MOF and HPW@CoCe-MOF. SEM images of HPW@CoCe-MOF showed a long strip structure with 1 μm length and smooth surface that changed to ~200 nm in size and rod-like structure after calcination. The porous nature of HPW@CoCeO composite was indicated by TEM images and uniform distribution of HPW onto the porous material was further validated. The BET surface area and average pore diameter of HPW@CoCe-MOF were obtained as 9.9 m²/g and 24 nm respectively. HPW@CoCeO exhibited BET surface area and pore diameter of 20.5 m²/g and 16 nm. The strong Brønsted acid of HPW was indicated from NH₃-TPD analysis. When HPW@CoCeO was utilized for the esterification of oleic acid with methanol, 67.2% conversion was obtained. The ORCs were 1:30 of oleic acid to methanol ratio, 10 wt% of

catalyst loading, and 60 °C of temperature in 4 h of reaction time. The conversion decreased from 67.2% to 61.8% in the eighth consecutive cycle indicating good reusability character.

Zhang et al. (2020d) synthesized a catalyst via a one-pot solvothermal method for the esterification of lauric acid with methanol. They prepared the catalyst by doping Zr-based MOF (UiO-66) with ammonium and Ag and named the catalyst as Ag₁(NH₄)₂PW₁₂O₄₀/UiO-66. Ag₁(NH₄)₂PW₁₂O₄₀/UiO-66 exhibited cubic crystal morphology with a large surface area of 554.7 m²/g and good thermal stability. The highest conversion of 75.6% was observed under ORCs of 15:1 of methanol to lauric acid, 10 wt% of catalyst concentration, and 150 °C of the reaction temperature in 3 h of reaction time. The reusability of the catalyst was done 6 times. A reduction in lauric acid conversion of 54.6% was observed at the 6th cycle due to the leaching of the catalyst. The Ea was found to be 35.2 kJ/mol and the reaction was of pseudo-first-order kinetics.

In another study, Zhang et al. (2019a) synthesized a stable solid acid catalyst by incorporation of heteropolyacids to MOFs by one-pot method and applied for the esterification of oleic acid. The prepared catalyst was PMA/Fe-BTC (PMA-Phosphomolybdic acid). The catalyst recorded the highest conversion of 72.3% under the ORCs of 16:1 of MTOAR, 10 wt% of catalyst loading, and 3 h of reaction time at 160 °C. The catalyst was reused up to 6 times resulting 59.2% of conversion which demonstrated good catalytic stability. The kinetic study revealed that the reaction was pseudo first-order with Ea of 49.5 kJ/mol.

Zhang et al. (2019b) prepared a catalyst by encapsulating silicotungstic acid (HSiW) on MOF (UiO-66) via the one-pot hydrothermal method. The prepared catalyst was HSiW-UiO-66. It was observed that the specific surface areas of UiO-66 and HSiW-UiO-66 were 667.2 m² g⁻¹ and 758.3 m² g⁻¹, respectively. The XRD and FT-IR analysis indicated that the HSiW was well-incorporated into the pores of UiO-66. During the esterification, HSiW-UiO-66 as the active catalyst showed the highest conversion of 80.5% under ORCs of 20:1 of methanol to lauric acid, 7 wt% of catalyst amount, and 4 h of reaction time at 160 °C. The RSM showed a conversion of 92.8% under the ORCs. Reusability analysis of the catalyst showed that catalyst could be reused up to 6th cycles. The study indicated that the encapsulation of HSiW into UiO-66 improved lauric acid conversion and showed high stability. The kinetic study suggested pseudo-first order reaction and showed a low Ea value of 27.5 kJ/mol.

In another study, Zhang et al. (2020a) investigated MOF encapsulated Zr-doped POM nano-hybrids as catalysts (ZrSiW/Fe-BTC and ZrSiW/UiO-66) for the synthesis of biodiesel via esterification. BET

isotherm indicated the larger pore size and larger surface area for ZrSiW/Uio-66 than that of ZrSiW/Fe-BTC. ZrSiW/Uio-66 was found to be thermally more stable than ZrSiW/Fe-BTC which was accounted for by the slow decomposition of organic ligands that began at 500–600 °C. ZrSiW/Uio-66 was observed to be more acidic than ZrSiW/Fe-BTC. Both the catalysts were investigated for the esterification of oleic acid using methanol. The ORCs were found out to be 20:1 MTOAR, 0.24 g of catalyst amount, 150 °C of reaction temperature, and 4 h of reaction time. Under these conditions, ZrSiW/Uio-66 and ZrSiW/Fe-BTC responded to 98.0% and 85.5% of oleic acid conversion, respectively. The reusability studies of ZrSiW/Uio-66 and ZrSiW/Fe-BTC catalysts revealed that the catalyst could be reused up to 6th cycles with 88.9% and 79% conversion, respectively.

Zhang et al. (2021a) recently synthesized a series of nanoporous hybrid materials using Zr supported MOF (UiO-66) for the esterification of oleic acid with methanol. The prepared materials were HSiW@ZrO₂-300, HSiW@ZrO₂-400, and HSiW@ZrO₂-500 which were calcined at 300, 400, and 500 °C for 2 h, respectively. They were collectively named HSiW@ZrO₂-T. The structural morphology of HSiW@UiO-66 was found to have an octahedral structure with a crystal size of 50–200 nm. HSiW@ZrO₂-T showed uneven spherical shapes with increased crystal size of 0.2–1.0 μm. The BET analysis showed that the surface areas of HSiW@UiO-66 and HSiW@ZrO₂-300 were 758.3 m²/g and 338 m²/g, respectively, which indicated that surface area reduced after calcination. The acidity of HSiW@ZrO₂-300 was analyzed by the NH₃-TPD technique which showed a high acid capacity of 6.2 mmol/g. During esterification, the maximum oleic acid conversion was 94.0% under the ORCs of 20:1 of MTOAR and 0.15 g of catalyst amount at 160 °C in 4 h. The catalyst showed good reusability and could be reused up to the 9th cycle. They also esterified highly acidic non-edible JCO which resulted in 81.8% of oil conversion.

Zhang et al. (2021b) synthesized a series of Keggin heteropoly acid (HSiW-Silicotungstic acid, HPMo-Phosphomolybdic acid, HPW-Tungstophosphoric acid) catalysts and performed oleic acid esterification using methanol. The catalysts were HPMo/Ni-MOF, HPW/Ni-MOF, and HSiW/Ni-MOF. TPD-NH₃ analysis showed that HPMo/Ni-MOF was highly acidic. The surface area and pore diameter of this catalyst was found to be 203.5 m²/g and 6.5 nm, respectively. This catalyst was applied for the esterification and ORCs were 20:1 of MTOAR, 3 wt% of catalyst amount, and 5 h of reaction time at 160 °C resulting in 86.1% of oleic acid conversion. The kinetic study suggested pseudo first-order kinetics with Ea of 64.6 kJ/mol. The catalyst could be reused up to the 10th cycle indicating good stability.

Zhang et al. (2021f) conducted another study to synthesize a novel composite catalyst (Keggin-PW₁₂@Uio-66) by encapsulating a heterogeneous catalyst to MOF via the solvothermal method. The catalyst was used for the esterification and transesterification of soybean oil. The ORCs noted for this reaction were 200 mg of catalyst amount, 5.5 ml of methanol, 1 g of soybean oil, and 4 h of reaction time at 75 °C. They reported more than 90% of oil conversion. The catalyst was highly stable and could be reused up to the 10th cycle. The study showed that the catalyst was structurally and thermally stable and also had good catalytic activity even after the 4th week.

Zhang et al. (2021e) developed a solid acid catalyst by incorporating HPMo on Cu-BTC (HPMo/Cu-BTC) using a one-pot hydrothermal method. During the esterification of oleic acid, the ORCs obtained were 7 wt% of catalyst amount, 20:1 of MTOAR, 160 °C of temperature, and 4 h of reaction time, and this revealed 93.7% of oleic acid conversion. The reaction obeyed pseudo first order kinetic with Ea of 37.5 kJ/mol. HPMo/Cu-BTC could be recycled up to 7 times with >80% of conversion. Utilization of this catalyst for the esterification of non-edible oil with high FFA showed high activity and produced >90% conversion.

Du et al. (2013) synthesized hexadecanuclear heteropolyoxozincate organic framework (IFMC-200) which consisted of 3, 4, 24-single node connected metal cluster with Lewis acidity. IFMC-200 was found to have a cubic shape, hydrophobic cages, and high thermal stability. The

esterification was carried out at 10:1 of alcohol to fatty acid ratio at 65 °C. Palmitic acid gave the highest conversion of 44.7% with 1 wt% of catalyst amount. The conversion with IFMC-200 showed 10 times higher conversion than the reaction that involved no catalyst. The catalyst could be reused up to the 6th cycle with no loss of the activity.

Li et al. (2021b) modified UiO-66(Zr) by incorporating *p*-toluene sulfonic acid (PTSA) to achieve an efficient solid acid catalyst for biodiesel synthesis. The prepared catalyst (UiO-G) was found to be the most active due to its double acid nature (Brønsted acid and Lewis acid) as well as the large surface area of 567.71 m²/g. During esterification of oleic acid, UiO-G showed 91.3% of conversion under the ORCs of MTOAR of 10:1, 70 °C of reaction temperature, 8 wt% of catalyst amount, and 2 h of reaction time. The activity of the catalyst reduced from 76.65% on its third cycle to 66.6% on its fourth cycle. Moreover, the kinetic study showed the Ea value of 28.94 kJ/mol with average reaction order of 1.51.

Ben-Youssef et al. (2021) applied heterogeneous acid catalyst (MOF-5) for the esterification and transesterification of JCO and WCO. RSM predicted the ORCs for WCO to be 0.75 wt% of catalyst dosage, 36:1 of MTOAR, 145 °C of reaction temperature, and 12 h of reaction time yielding 90.8% of biodiesel. The predicted ORCs for JCO were 0.75 wt% of catalyst dosage, 36:1 of MTOAR, 145 °C of reaction temperature, and 9.59 h of reaction time resulting in 88.3% of the product. It was found that the experimental yield was 10% lower than the predicted yield. WCO was found better than JCO. WCO was used to study the reusability of the catalyst. The catalyst could be reused till the 3rd cycle and during the first two cycles, the yield reduced from 82.01% to 41.2%, and the yield reduced to 20.2% in the third cycle.

Ye et al. (2019) proposed a strategy to introduce ionic liquids (ILs) into MOFs. They synthesized a Brønsted-Lewis acidic catalyst, [(CH₂COOH)₂IM]H₂SO₄@H-UiO-66, using bidentate coordination. The prepared catalyst was used for biodiesel synthesis via esterification of oleic acid with methanol. The catalyst was found to have a crystalline structure with a surface area of 748 m²/g and high activity due to Brønsted acidic and Lewis acidic nature. RSM predicted the ORCs which were 6.28% of catalyst amount, MTOAR of 10.39:1, reaction temperature of 80 °C, and reaction time of 5 h resulting in 93.71% of biodiesel yield, and 93.82% was the experimental yield. The catalyst showed good reusability up to the 5th cycle.

Zhang et al. (2020e) developed a catalyst from MIL-100(Fe) encapsulated by H₄SiW via the hydrothermal method and studied its catalytic activity for the esterification of lauric acid. The catalyst H₄SiW/MIL-100(Fe) was synthesized successfully and contained a cube-like structure with a size of about 300 nm. The optimum lauric acid conversion was found out to be 80.3% at lauric acid to methanol ratio of 1:12, temperature of 160 °C, 0.3 g of catalyst concentration, and reaction time of 3 h. The catalyst could be reused up to the 11th cycle that maintained >60% conversion.

Peña-Rodríguez et al. (2018) synthesized acid heterogeneous catalyst, Co(II)-MOF. Ultrasound-assisted transesterification of *Erythrina mexicana* oil was done using the catalyst. The reaction was carried out by treating 10:1 MTOAR and 25 mg of catalyst in Teflon cap at 60 °C for 12 h resulting in 80% of oil conversion. The catalytic activity was due to the free carboxylic acid gaps in the structure.

Xie and Wan (2019b) synthesized a catalyst by fabricating MIL-100(Fe) MOFs with heteropolyanion-based ionic liquids (ILs). The prepared catalyst AIL/HPMo/MIL-100(Fe) was applied for transesterification of soybean oil as well as esterification of oleic acid with methanol. The catalyst was found to be highly active due to the synergistic effect of Lewis acid and Brønsted acid sites. Under ORCs (Table 3), 92.3% of soybean oil conversion was received and esterification of 20% of oleic acid dissolved soybean oil reported 100% conversion. The catalyst could be reused up to the 5th cycle resulting in 90.3% conversion at the end.

Xie et al. (2021) prepared H₆PV₃MoW₈O₄₀/Fe₃O₄/ZIF-8 catalyst and it was found to be thermally stable exhibiting a high surface area and

superparamagnetic nature. Transesterification of soybean oil resulted in a maximum conversion of 92.6% under ORCs of 30:1 of MTOR and 6 wt % of catalyst concentration at 160 °C of temperature in 10 h. The esterification of low-grade oil with 20 wt% of oleic acid resulted in a 100% conversion under similar conditions. Due to the decomposition of active sites, the catalyst could be reused for five runs and 80.4% of oil conversion was reported.

2.2. Basic MOF catalyzed biodiesel production

Many alkali and alkaline earth metal oxides, and basic ionic liquids have been employed as solid heterogeneous base catalysts for biodiesel synthesis. Moreover, some supported base catalysts such as alumina, silica, zirconia, etc. are also applied to enhance the surface area and catalytic activity and to lessen the production price (Tantirungrotechai et al., 2013). However, the solid base catalysts are also associated with a high temperature and high reaction time for conversion of the product (Li et al., 2011). Additionally, the leaching of the active sites from the solid catalyst remains a prime concern. This can be significantly avoided by making use of MOF materials. The structure and properties of MOFs can be facilely modified via the coordination of basic functional groups. Since the MOFs can strongly bind the incorporated groups into their structure, the risk of active site leaking is reduced and thus the transesterification reaction can be performed effortlessly (Ma et al., 2021). The catalytic performances and efficiencies of different basic MOF catalysts in biodiesel synthesis are shown in Table 4.

In a study, Chen et al. (2014) utilized amine-functionalized MOF materials as a solid base catalyst for transesterification of triglyceride. The MOF materials were synthesized in two different ways viz. (a) dative modification of unsaturated metal sites located at the secondary building units (SBUs) of MOFs and (b) covalent modification of the organic linkers within the MOF by alkylation with 2-dimethylaminoethyl chloride. The series of amino-functionalized MOF composites prepared were MOF-5-ED, MOF-5-DMAP, IRMOF-10-ED, IRMOF-10-DMAP, MIL-53(Al)-NH₂, and MIL-53(Al)-NH-NMe₂. The surface areas of MOF-5-ED

and MOF-5-DMAP were found to be 391 m²/g and 348 m²/g, respectively. When the catalytic activities of all these catalysts were compared, the best result obtained was >99.9% conversion for IRMOF-10-ED, MOF-5-ED, and MIL-53(Al)-NH-NMe₂ at the ORCs of 30 mg of catalyst, 1 ml of methanol, 181 mg of glyceryl triacetate, and at 50 °C in 3 h, 3 h, and 4 h respectively. The basic site densities for IRMOF-10-ED, MOF-5-ED, and MIL-53(Al)-NH-NMe₂ were obtained as 0.81, 0.76, and 0.65, respectively. The kinetic study revealed the first-order kinetics with 48.2 kJ/mol of activation energy. The solid base catalyst synthesized in this study exhibited high catalytic efficiency for liquid phase transesterification.

Fazaeli and Aliyan (2015) utilized ZIF (Zeolite imidazolate framework)-8 MOFs as catalyst support for the transesterification of soybean oil. ZIF-8@GO (GO-Graphene oxide) was first prepared as a hybrid nanocomposite via the one-pot encapsulating method. Thereafter, the hydrothermal treatment of ZIF-8@GO and 10 M alkali solution of both NaOH and KOH was performed to synthesize KNa/ZIF-8@GO catalyst. The BET surface area, the pore volume, and pore diameter of KNa/ZIF-8@GO were obtained as 365 m²/g, 0.131 cm³/g, and 2.85 nm, respectively which were lower than that of ZIF-8, indicating the incorporation of Na and K into porous ZIF-8. In the study, 98% conversion of biodiesel was achieved under ORCs of 18:1 of MTOR, 8 wt% of catalyst loading, 0.05 wt% of (K atoms) K loading at 100 °C, and 3 h of reaction time.

Xie and Wan (2018) studied a magnetically recyclable solid catalyst for biodiesel production from soybean oil as a clean and eco-friendly process. They first prepared Fe₃O₄ NPs (nanoparticles) via the solvothermal method. The prepared core of Fe₃O₄ was coated with porous HKUST-1 type MOFs through a Layer-by-Layer assembly method, and thereby the core-shell magnetic Fe₃O₄@HKUST-1 material was fabricated. The solid base catalyst Fe₃O₄@HKUST-1-ABILs was prepared by immobilizing amino-functionalized ionic liquids onto the magnetically responsive Fe₃O₄@HKUST-1 composite. The BET surface area of the composite Fe₃O₄@HKUST-1 was found to be 237.6 m²/g. However, the surface area and pore volume decreased to 23.7 m²/g and 0.15 cm³/g

Table 4
Catalytic performance of different basic MOFs catalysts.

Biodiesel feedstock/Alcohol	Catalyst	Catalyst preparation method	Biodiesel synthesis method	Surface area (m ² g ⁻¹)	Reaction conditions					Reference
					ATOR	Catalyst (wt %)	Temp (°C)	Time (h)	Conversion (%)	
GTA/methanol	IRMOF-10-ED	-	Transesterification	-	10:1.81	16.6	50	3	>99.9	Chen et al. (2014)
GTA/methanol	MOF-5-ED	-	Transesterification	391	10:1.81	16.6	50	3	>99.9	Chen et al. (2014)
GTA/methanol	MIL-53(Al)-NH-NMe ₂	-	Transesterification	-	10:1.81	16.6	50	4	>99.9	Chen et al. (2014)
SO/methanol	KNa/ZIF-8@GO	Hydrothermal method	Transesterification	365	18:1	8	100	3	98	Fazaeli and Aliyan (2015)
SO/methanol	Fe ₃ O ₄ @HKUST-1-ABILs	Solvothermal method	Transesterification	23.7	30:1	1.2	Reflux temp	3	92.3	Xie and Wan (2018b)
SO/methanol	ZIF-90-Gua	Solvothermal method	Transesterification	830.4	15:1	1	65	6	95.4	Xie and Wan (2019c)
PO/methanol	MM-SrO	Mechanical mixing method	Transesterification	66.88	12:1	8	65	0.5	96.19	Li et al. (2019)
PO/methanol	Fe@C-Sr	<i>In-situ</i> method	Transesterification	68.93	9:1	4	65	0.5	98.12	Li et al. (2020a)
SO + SFO/methanol	NaOH/magnetized ZIF-8	-	Transesterification	0.0005	21:1	3	65	1	100	Abdelmigeed et al. (2021)
WCO/methanol	Zr-fumarate-MOF (MOF-801)	Solvothermal method	Transesterification	750.11	50 wt%	10	180	8	60	Shaik et al. (2022)
PO/methanol	UCA700	Hydrothermal method	Transesterification	3.44	9:1	8	65	1	92.94	Li et al. (2022)
PO/methanol	UCN650	Hydrothermal method	Transesterification	24.06	9:1	6	65	1	96.99	Li et al. (2022)
SO/methanol	20MgO@Zn-MOF-370	Self-assembly, encapsulation	Transesterification	1048.5	3:1	1	210	2	67.6	Yang et al. (2022)
SO/methanol	20MgO@ZnO-400	Self-assembly, encapsulation	Transesterification	32.6	3:1	1	210	2	73.3	Yang et al. (2022)

ATOR-Alcohol to oil ratio; wt-weight; Temp-temperature; h-hour; SO-Soybean oil; PO-Palm oil; GTA-Glyceryl triacetate; SFO-Sunflower oil.

respectively for $\text{Fe}_3\text{O}_4\text{@HKUST-1-ABILs}$ which might be due to the bonding of ABILs on $\text{Fe}_3\text{O}_4\text{@HKUST-1}$ support. The saturation magnetization value of $\text{Fe}_3\text{O}_4\text{@HKUST-1-ABILs}$ was determined to be 18.28 emu/g. The catalytic activity of $\text{Fe}_3\text{O}_4\text{@HKUST-1-ABILs}$ was investigated through the transesterification of soybean oil. In the reaction, the maximum conversion of 92.3% was obtained under the ORCs of 30:1 of MTOR and catalyst dosage of 1.2 wt% after 3 h at the reflux temperature of methanol. When the recycling experiment was performed, no significant reduction in oil conversion was observed even after several consecutive reaction cycles indicating a good reusability feature of the catalyst.

ZIF-90, despite having high stability and large surface area, cannot be employed directly as a catalyst due to the lack of catalytic activities. To address this issue, Xie and Wan (2019c) fabricated the MOFs and introduced a post-functionalized solid base catalyst denoted as ZIF-90-Gua (Gua–Guanidine) (Fig. 12) for the transesterification of soybean oil. ZIF-90 was post-functionalized with organic guanidine via an imine condensation reaction to form covalent bonds. Guanidine was used and acted as a strong base and could be suitably anchored onto the porous support via covalent bond providing long-term catalytic activities for the catalyst. The catalyst was prepared via various methods such as $\text{H}_2\text{O}/\text{PVP}$ (polyvinylpyrrolidone) method, solvothermal method, and sodium formate-based synthesis method. The XRD pattern of ZIF-90 obtained from the solvothermal method exhibited good crystallinity and high phase purity as compared to ZIF-90 obtained from the other two methods. The BET surface area of the ZIF-90 (solvothermal), ZIF-90 ($\text{H}_2\text{O}/\text{PVP}$), and ZIF-90 (sodium formate) samples were found to be 830.4, 752.3, and 737.5 m^2/g , respectively. The SEM technique was applied to study the morphological characters of the catalyst and the SEM images are shown in Fig. 13. The revealed the spherical shape of ZIF-90 with a mean particle size diameter of 3 μm . It was observed that the ZIF-90-Gua catalyst showed similar morphology to that of ZIF-90 even after its modification with guanidine, which could provide a better approachability to the active sites. The reaction with the catalyst could provide 95.4% conversion under the ORCs of 15:1 of MTOR, 1 wt % of catalyst dosage, 65 °C of reaction temperature, and 6 h of reaction time. The reusability showed no significant reduction in catalytic activity up to the 5th cycle of reaction.

Li et al. (2019) prepared MIL-Fe-supported MOF by hydrothermal method and applied it as a suitable catalyst for transesterification. The catalytic activity of SrO was studied in their experiment supported by MIL-Fe since SrO exhibits inferior pore structure and reusability when employed as a catalyst alone. The required catalyst was prepared by using MOF to support strontium carbonate via the *in-situ* titration method (ST) and mechanical mixing method (MM). Calcination under inert atmosphere was done in both the aforementioned method to produce magnetic catalysts which were named ST-SrO and MM-SrO, respectively. The surface area and pore volume of MM-SrO were determined to be 66.88 m^2/g and 0.14 cm^3/g , respectively. Similarly, these were found to be 72.59 m^2/g and 0.13 cm^3/g , respectively for ST-SrO. The total basicity for ST-SrO and MM-SrO were determined to be 1.94 and 2.21 mmol/g, respectively. When the reaction was performed with palm oil and methanol, MM-SrO contributed a good result of 96.19% conversion with 8 wt% of catalyst loading, MTOR of 12, and at

65 °C of the reaction temperature in 30 min. After the third cycle of the reaction, the conversion was maintained at 82.49% under the same conditions. The saturation magnetization of MM-SrO and ST-SrO were obtained as 110.6 and 103.2 emu/g, respectively, leading to easy separation from the mixture by a magnet.

Li et al. (2020a) utilized MIL-Fe(100) composite to synthesize magnetic mesoporous support (Fe@C) via carbonization for transesterification of palm oil with methanol. MIL-Fe(100) was first synthesized by the hydrothermal method which was later carbonized to prepare magnetic support. Afterward, the heterogeneous base catalyst (Fe@C–Sr) was produced by dispersing SrO on Fe@C via the *in-situ* method. The optimum SrO loading and activation temperature was obtained as 30 wt% and 900 °C respectively. The highest basicity of 7.94 mmol/g was obtained when 30 wt% of SrO was loaded on Fe@C with basic strength of $9.8 < \text{H}_\text{L} < 15$. The surface area and pore volume of Fe@C–Sr were measured as 68.93 m^2/g and 0.12 cm^3/g respectively. The average pore diameter of Fe@C–Sr was found to be 7.07 nm. The saturation magnetization of Fe@C–Sr was reported to be 86.76 emu/g. The maximum conversion of 98.12% was obtained with the ORCs of 9:1 of MTOR, and 4 wt% of catalyst loading at 65 °C in 0.5 h. After the third cycle of reaction, the conversion remained 80.59% showing good reusability character.

Abdelmigeed et al. (2021) employed a magnetized ZIF-8 catalyst impregnated with NaOH for biodiesel production. The oil feedstock used was 1:1 M ratio of soybean and sunflower oils with an acid value of 0.16 mg KOH/g. The specific surface area, average particle size, and average pore diameter of the catalyst were 500 mm^2/g , 300 nm, and 1.1 nm, respectively. The transesterification of oil with methanol was carried out and further, the catalyst reusability was investigated. Several techniques such as RSM and factorial design were applied to study the influences of catalyst dose and MTOR during the conversion. The complete conversion (100%) was obtained using 21:1 of MTOR, 3 wt% of catalyst dosage, 65 °C of reaction temperature, and 1 h of reaction time. The best-suited model was determined to be the two-factor interaction model with a determination coefficient (R^2) of 0.97. The kinetics of methanolysis was satisfied by the pseudo-second order model. The properties of the biodiesel obtained from the experiment agreed with the ASTM standard. The cetane number, flash point, and cloud point of the biodiesel were found to be 65, 140 °C and -5 °C respectively. The calcination at 200 °C under an inert atmosphere was done to improve the interaction of magnetized ZIF-8 with NaOH which then maintained the conversion up to 90% in the second reaction cycle.

Shaik et al. (2022) synthesized a fumarate-based MOF (MOF-801) catalyst and performed the reaction of used vegetable oil with methanol. They reported a maximum conversion of ~60% using 10 wt% of catalyst concentration, and 50 wt % of MTOR at 180 °C for 8 h. The catalyst could be reused up to the 3rd reaction cycle with a 10% decrease in the product.

In another study, Li et al. (2022) synthesized calcium-acetate supported UiO-66(Zr) catalyst (UCA700 activated in air, UCN650 activated in N_2) for transesterification of palm oil. The surface area and pore volume of UCN650 were much higher than UCA700 favoring the transesterification reaction. UCN650 reported higher oil conversion (96.99%) at MTOR of 9:1 and catalyst amount of 6 wt% at a reaction

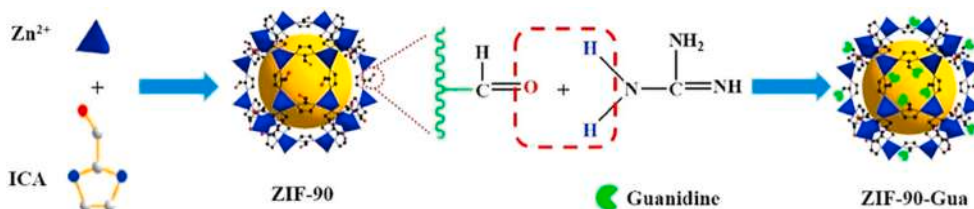


Fig. 12. Preparation of a porous catalyst, ZIF-90-Gua. Reproduced from reference (Xie and Wan, 2019c) with permission of Elsevier, Copyright © 2019 (License no. 5263670028576).

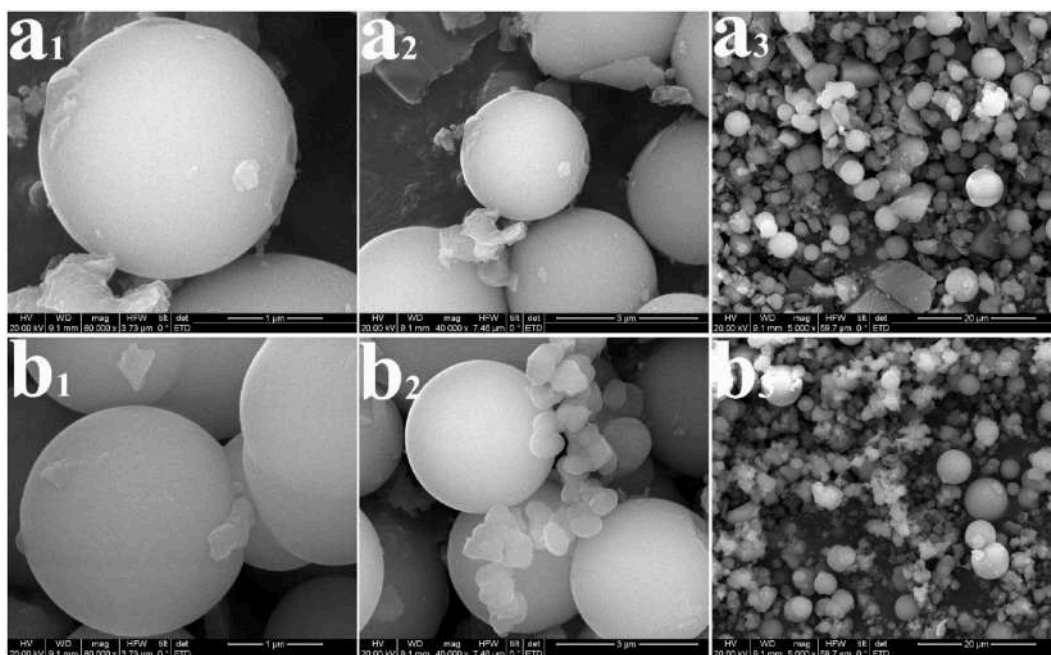


Fig. 13. SEM images of ZIF-90 (a_1 , a_2 , and a_3) and ZIF-90-Gua catalyst (b_1 , b_2 , and b_3). Reproduced from reference (Xie and Wan, 2019c) with permission of Elsevier, Copyright © 2019 (License no. 5263670028576).

temperature of 65 °C in 1 h. UCA700 recorded lower oil conversion (92.94%) under the conditions of 9:1 MTOR, 8 wt% of catalyst concentration, 65 °C of reaction temperature, and 1 h of reaction time. The catalysts were reused up to the 3rd reaction cycle.

Yang et al. (2022) utilized MOF-based Mg–Zn nanocatalysts (20MgO@Zn-MOF-370 and 20MgO@ZnO-400) in the transesterification of SO. The synthesized pathways of MOF hybrid nanocatalysts are shown in Fig. 14. 20MgO@Zn-MOF-370 showed a larger BET surface area of 1048.5 m²/g than 20MgO@ZnO-400. The microscopic analyses of the prepared nanocatalysts are shown in Fig. 15. Fig. 15a showed ultrafine and small MgO crystallites of ~5 nm. The Mg atoms were not distributed on the framework but observed only in the Zn-MOF material. Fig. 15b showed the more irregular materials with deposition of a large portion of the MgO particles at the outer surface of Zn-MOF. Fig. 15c indicated the successful preparation of MgO@ZnO nanostructure with the uniform distribution of ZnO and MgO nanocrystallites (Fig. 14, Route B). The transesterification was carried out at ORCs of the catalyst amount of 1 wt%, MTOR of 3, reaction temperature of 210 °C, and reaction time of 2 h 20MgO@Zn-MOF-370 could provide 67.6 ± 6.2% of oil conversion, whereas 20MgO@ZnO-400 produced

73.3 ± 1.3% of oil conversion. The catalysts were reused up to the 3rd cycle.

2.3. Enzyme-based MOF catalyzed biodiesel production

The transesterification and esterification reactions can also be catalyzed by an enzyme besides alkali and acid catalysts. Some notable limitations can be observed in the case of alkali and acid-catalyzed reactions of biodiesel production. Although these may produce high yields, they consume an immense amount of energy as the reaction is endothermic. Moreover, the triglycerides with high FFAs should be avoided during such a reaction as they may end up forming soap, leading to difficulty in the separation of the desired product. The enzyme, being ecofriendly and non-toxic, acts as a biocatalyst in the reaction. In contrast to chemically catalyzed transesterification reactions, enzyme-catalyzed reactions consume less energy and offer no recovery issues of glycerol, enabling reactions with high FFA contents with high selectivity. However, they exhibit a few noteworthy shortcomings as well. Enzyme catalysts show frail resistance to alcohol, time-consuming, poor reusability and the grueling separation process make it lavish (Bajaj

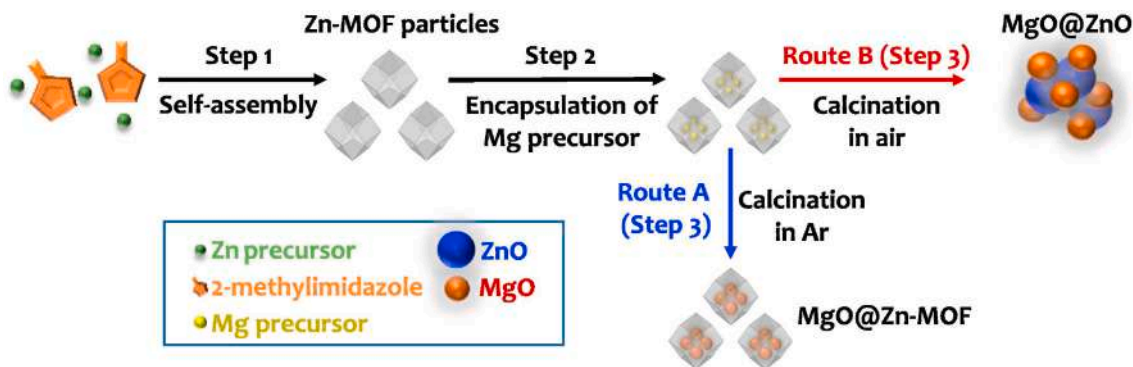


Fig. 14. Syntheses of MOF-based Mg–Zn nanocatalysts. Route A: MgO nanomaterials encapsulated in Zn-MOF (MgO@Zn-MOF). Route B: MgO nanomaterials decorated on ZnO nanomaterials (MgO@ZnO). Reproduced from reference (Yang et al., 2022) with permission of Elsevier, Copyright © 2022 (License no. 5263670769079).

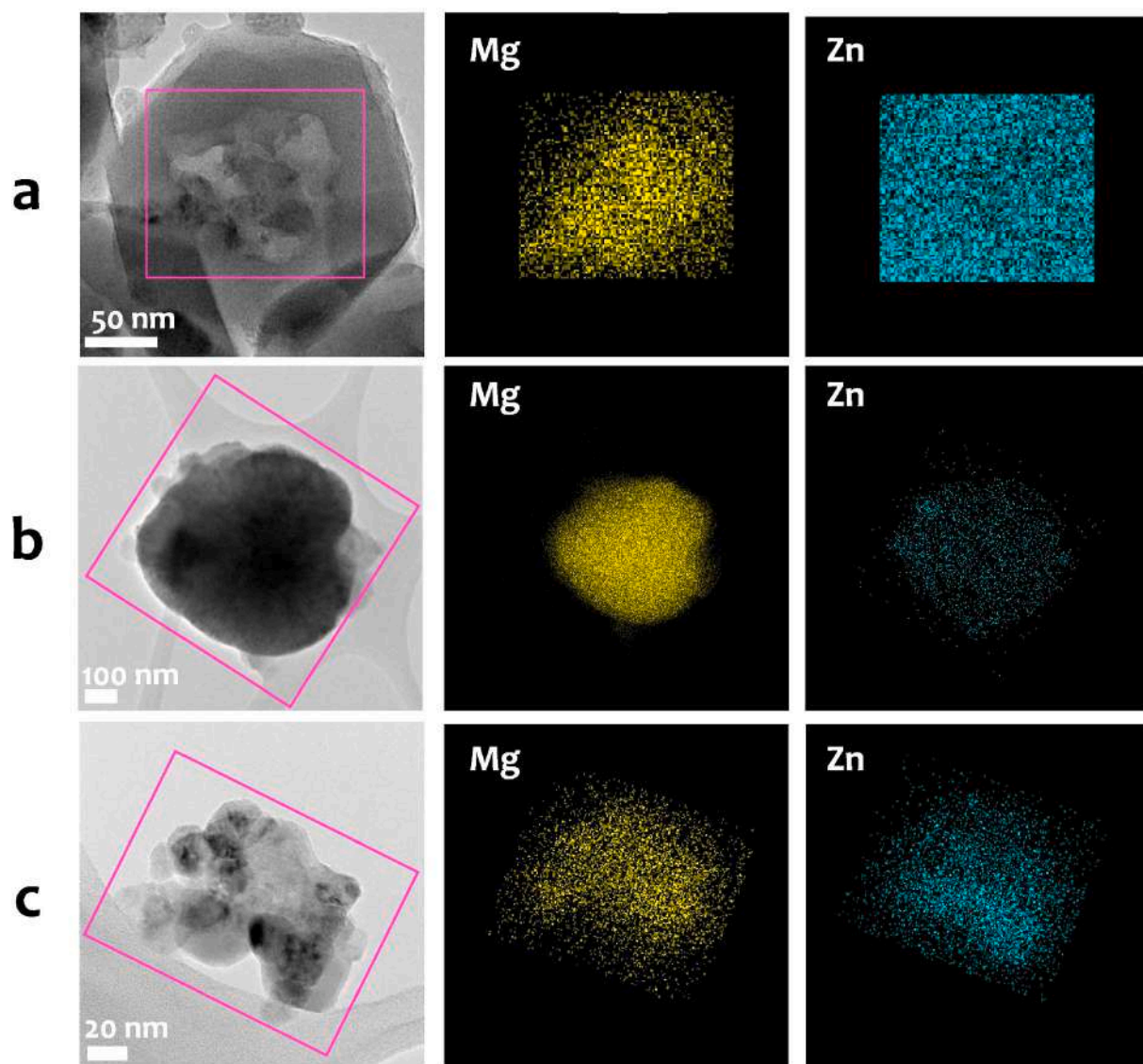


Fig. 15. TEM image with elemental mapping of 20MgO@Zn-MOF-400 (a), 40MgO@Zn-MOF-400 (b), and 20MgO@ZnO-400 (c). Reproduced from reference (Yang et al., 2022) with permission of Elsevier, Copyright © 2022 (License no. 5263670769079).

et al., 2010; Ma et al., 2021). To alleviate the separation process and upgrade their stability, MOFs have drawn the attention of researchers. On account of having high surface area, versatile pore size, and feasible anatomy, MOFs have been utilized as a support for enzyme immobilization. The immobilization of enzymes or lipases on MOF composites can be achieved via numerous methods such as encapsulation, adsorption, and covalently attached and cross-linking method (Shomal et al., 2021). The versatile characteristics of the solid support MOFs can enhance the lifetime of the enzyme and retain the catalytic activity to undergo better transesterification and esterification reactions. In Table 5, the performances of different enzyme-based MOF catalysts utilized in biodiesel synthesis are summarized.

In the transesterification process of soybean oil with ethanol, Liu et al. (2017) utilized the nanoporous carbon (NPC) derived from MOFs as a catalyst to lower the reaction time and to improve the catalytic efficiency. To achieve this, they first developed COOH functionalized NPC which was derived from MOF via direct pyrolysis and named carbonized MOF (cMOF). The solid support cMOF was thereafter immobilized with *Burkholderia cepacia* lipase (BCL) which was then used for biodiesel production. Series of cMOF were synthesized viz. cMIL-100 (Al)-600, cMIL-100(Al)-800, and cMIL-100(Al)-900 from direct

pyrolysis of MIL-100(Al). The amount of COOH for cMIL-100(Al)-600, cMIL-100(Al)-800, and cMIL-100(Al)-900 was estimated to be 2.79, 1.86, and 2.29 mmol/g, respectively. Langmuir surface area of cMIL-100 (Al)-800 was found to be 502 m²/g. The enzyme BCL was immobilized for all cMIL-100(Al)-600/800/900 and the resultant catalysts were denoted as BCL@cMIL-100(Al)- 600/800/900. It was found that BCL loading efficiency decreased from 27.5% to 20.4% with increasing carbonization temperature from 600 to 900 °C, while the catalytic efficiency significantly reduced from 72.6% to 23.5%. cMIL-100(Al)-600 and cMIL-100(Al)-800 showed comparable efficacies for the 1st catalytic cycle with 72.6% and 80.3% yield, respectively. But after the 9th cycle of reaction, cMIL-100(Al)-600 obtained 66.3% yield while only 43.3% yield was obtained using cMIL-100(Al)-800. The COOH in cMIL-100(Al)-600 enhanced the hydrogen bond between the enzyme and the support thereby improving the catalytic efficiency. The biodiesel production from soybean oil with ethanol using BCL@NPCs or BCL@MIL-100(Al) was done at 40 °C for 12 h.

Rafei et al. (2018) studied the activity of *Candida rugosa* lipase immobilized on MOF support in catalyzing biodiesel synthesis. The MOF composite used in the experiment was ZIF-67 which is composed of cobalt as metal cations and 2-methylimidazolate anions as a bridging

Table 5
Catalytic performance of different enzymatic MOFs catalysts.

Biodiesel feedstock/Alcohol	Enzyme	Catalyst	Catalyst preparation method	Biodiesel synthesis method	Surface area (m ² g ⁻¹)	Reaction conditions					Reference
						ATOR	Catalyst (wt %)	Temp (°C)	Time (h)	Product, Y or C (%)	
SO/ethanol	BCL	BCL@cMIL-100(Al)-600	–	Transesterification	–	–	–	40	12	72.6 (Y)	Liu et al. (2017)
SO/ethanol	BCL	BCL@cMIL-100(Al)-800	–	Transesterification	502	–	–	40	12	80.3 (Y)	Liu et al. (2017)
SO/methanol	<i>Candida rugosa</i>	Lipase@ZIF-67	Encapsulation	Transesterification	260	6:1	20	45	60	78 (Y)	Rafiei et al. (2018)
SO/ethanol	BCL	BCL-ZIF-8	Adsorption	Transesterification	–	4:1	6	40	12	93.4 (Y)	Adnan et al. (2018a)
SO/methanol	ANL	ANL/UiO-66-PDMS-6	Adsorption	Transesterification	–	–	2–5	45	24	88 (Y)	Hu et al. (2018)
SO/methanol	RML	RML@ZIF-8	Encapsulation	Transesterification	593.36	4:1	8	45	24	95.6 (Y)	Adnan et al. (2018b)
SO/methanol	<i>Candida rugosa</i>	Lipase-Fe ₃ O ₄ @MIL-100 (Fe)	Covalent bonding	Transesterification	36.43	4:1	25	40	60	92.3 (C)	Xie and Huang (2019a)
SFO/methanol	QLM isolated from <i>Alcaligenes</i> species	Lipase@Bio-MOF	Biomimetic mineralization	Transesterification	85.3	1:8	–	–	–	>60 (C)	Li et al. (2020b)
SO/methanol	AOL CJLU-31	AOL@PDMS-ZIF-L	Adsorption	Transesterification	–	4:1	2	45	24	94.37 (Y)	Zhong et al. (2021)
OA/methanol	CALB	Bio-based CALB@MOF	Encapsulation	Esterification	–	3.65:1	11.8	46.3	11.55	98.9 ± 0.4 (Y)	Liu et al. (2021)
JCO/methanol	RML	RML@Fe ₃ O ₄ @COF-OMe	Coprecipitation	Transesterification	–	0.45:0.15	0.5 mg	50	48	67.8 (Y)	Zhou et al. (2021)
SO/methanol	ANL	ANL@M-ZIF-8-PDMS	CVD method	Esterification	–	4:1	2–5	45	24	88 (Y)	Hu et al. (2020b)
RCO/methanol	<i>Enterobacter cloacae</i> lipase	Zr-MOF/PVP	Electro-spinning method	Ultrasound- assisted transesterification	1928	3:1	0.67	–	12	83 (C)	Badoei-Dalfard et al. (2021)
SO/methanol	ANL	ANL@M-ZIF-8	Direct diffusion method	Transesterification	1276	1.8:10	1	45	24	80 (Y)	Hu et al. (2021)
SO/methanol	ANL	ANL/ZIF-8	Surface immobilization method	Transesterification	–	1.8:10	7	45	12	65 (Y)	Hu et al. (2021)
Olive oil/methanol	<i>Eversa transform</i> 2.0	L@ZIF-8	Encapsulation	Transesterification	666.3	6:1	20	40	4	>50 (Y)	Al-Mansouri et al. (2022)
Olive oil/methanol	<i>Thermomyces lanuginosus</i>	ZIF-67	Adsorption	Transesterification	1332.9	12:1	20	40	4	90 (C)	Shomal et al. (2022)
Olive oil/methanol	<i>Thermomyces lanuginosus</i>	ZIF-8	Adsorption	Transesterification	281.6	12:1	20	40	4	88 (C)	Shomal et al. (2022)
Olive oil/methanol	<i>Thermomyces lanuginosus</i>	HKUST-1	Adsorption	Transesterification	834.8	12:1	20	40	4	71.8 (C)	Shomal et al. (2022)

ATOR–Alcohol to oil ratio; wt–weight; Temp–temperature; C–conversion; Y–yield; h–hour; BCL–*Burkholderia cepacia* lipase; ANL–*Aspergillus niger* lipase; RML–*Rhizomucor miehei* lipase; CALB–*Candida antarctica* lipase B; AOL–*Aspergillus oryzae*; CVD–chemical vapor deposition; SO–Soybean oil; OA–Oleic acid; SFO–Sunflower oil; RCO–*Ricinus communis* oil.

ligand (Co(mim)₂). Thereby, a nano biocomposite lipase@ZIF-67 was prepared via the *in-situ* encapsulation method of *Candida rugosa* lipase on a ZIF-67 composite. Before and after washing off the lipase@ZIF-67, protein loading of 11.42 and 7.84 wt% respectively was found using the standard Bradford assay method. The BET surface area and pore volume of lipase@ZIF-67 were measured to be 260 m²/g and 0.32 cm³/g respectively. The enzyme immobilization increased the value of the average pore diameter of ZIF-67 from 2.3 to 5.03 nm. The transesterification of soybean oil with methanol was studied using the prepared biocatalyst in a solvent-free condition. Under the ORCs of 6:1 of ATOR, 100 mg of catalyst loading, 10% of water concentration, 45 °C of temperature, and 60 h of reaction time, biodiesel yield of 78% was obtained.

In a study, Adnan et al. (2018a) selected mesoporous hierarchical ZIF-8 as a support for the immobilization of BCL via the adsorption technique for the synthesis of the biocatalyst. In the beginning, a hierarchical micro-/mesoporous ZIF-8 was prepared in an aqueous solution using cetyltrimethylammonium bromide as a regulating liaison and amino acid (L-histidine) as a co-template. After that, BCL was immobilized on ZIF-8 under standard conditions via the adsorption method. Several randomly distributed mesopores on the surface of hierarchical ZIF-8 were identified with the help of TEM images. The XRD analysis showed a decrease in crystallinity of ZIF-8 after immobilization of BCL. The BET surface area of hierarchical ZIF-8 was found to be 751.87 m²/g. The XRD pattern revealed the reduction in ZIF-8 crystallinity after the immobilization. It was indicated that the activity recovery of an immobilized enzyme increased by 12-fold under ORCs of BCL-ZIF-8 loading of 700 mg, 25 °C of immobilization temperature, 30 min of adsorption time, and pH value of 7.5. When the immobilized BCL was used as a catalyst for the transesterification of soybean oil with ethanol, it showed a 93.4% yield. The reaction for maximum yield was done under the ORCs of 1:4 of molar ratio of oil to ethanol, 6 wt % of lipase dosage, 3% of water content, 40 °C of temperature, and 12 h of reaction time with three-step addition of alcohol at 4 h intervals. BCL-ZIF-8 showed 71.3% conversion yield after a continuous eight cycle of reaction which indicated the propitious feature of BCL-ZIF-8 catalyst to be used in biodiesel production.

In research conducted by Hu et al. (2018), a typical MOF UiO-66 was used as a support for the immobilization of *Aspergillus niger* lipase (ANL) and used in biodiesel production. They modified the UiO-66 composite by coating with facile PDMS adopting the chemical vapor deposition (CVD) method to induce a hydrophobic layer on the surface of the composite without compromising with their intrinsic properties. After that, the enzyme was directly immobilized on UiO-66-PDMS by surface physical adsorption forming hydrophobic interaction. The product so obtained, ANL/UiO-66-PDMS-6h, showed a similar crystalline structure to that of the parent UiO-66 composite. When the methanolysis of soybean oil was performed using ANL/UiO-66-PDMS-6h, 93% conversion was obtained in 24 h. The reusability analysis showed 83% catalytic activity after the 10th reaction cycle.

In the study conducted by Adnan et al. (2018b), ZIF-8 was employed as a carrier to immobilize *Rhizomucor miehei* lipase (RML) via a single-step encapsulation method. The resultant nanobiocatalyst RML@ZIF-8 was then utilized in the production of biodiesel from soybean oil with ethanol in an isoctane medium. Its BET surface area and pore size from Barrett–Joyner–Halenda method was found to be 593.36 m²/g and 4.65 nm respectively. The highest conversion yield of biodiesel reached 95.6% under the ORCs of 1:4 of oil to ethanol molar ratio, 8 wt% of lipase dosage, 45 °C of reaction temperature, and 24 h of reaction time. After the 10th consecutive cycle, the yield remained 84.7% maintaining the catalytic activity.

Xie and Huang (2019) employed core-shell structured MOF, Fe₃O₄@MIL-100(Fe) for *Candida rugosa* lipase mediated biodiesel synthesis from soybean oil. In the beginning, MIL-100(Fe) MOFs were smeared with carboxyl-functionalized Fe₃O₄ particles with the help of assembly method, in which Fe²⁺ cations of Fe₃O₄ interact with the

surface carboxyl groups of MIL-100(Fe) MOFs to initiate the growth of MOF shell. The surface area and pore volume of the lipase immobilized Fe₃O₄@MIL-100(Fe) were found to be 36.43 m²/g and 0.12 cm³/g respectively with a pore size of 6.88 nm. The transesterification of soybean oil was performed with the stepwise addition of methanol using an immobilized lipase catalyst. The highest biodiesel conversion of 92.3% was achieved under the ORCs of 4:1 of MTOR, and 25 wt% of catalyst loading at 40 °C of the reaction temperature in 60 h. When the reusability was examined, the catalyst maintained 83.6% activity after the 5th consecutive cycle without noteworthy loss of mass.

Li et al. (2020b) adopted the biomimetic mineralization method to fabricate biobased MOFs material (Fig. 16) by immobilizing a thermophilic lipase QLM isolated from *Alcaligenes* species and applied in biodiesel synthesis. Zinc acetate and adenine were employed as metal ion and biomolecular ligand respectively to synthesize lipase@Bio-MOF. The BET surface area was obtained as 85.3 m²/g. The morphology of the catalyst was studied using SEM and TEM techniques (Fig. 17), which showed the formation of the uniform spherical structure after the addition of lipase indicating its vital role played. Using the hydrolysis of *p*-nitrophenyl caprylate as a model, lipase@Bio-MOF showed high catalytic activity and stability at high temperatures, pH of about 7.5, and under alkaline conditions. The enzyme demonstrated high defense against Zn²⁺, Mn²⁺, Ni²⁺ and Cu²⁺ metal ions. A conversion of >60% was obtained when the prepared enzyme was used in the transesterification of sunflower oil with methanol at 8:1 of MTOR. The morphology and crystal structure of lipase@Bio-MOF remained unchanged even after the 3rd reaction cycle indicating its good recyclability.

Zhong et al. (2021) studied the catalytic activity of immobilized MOF by *Aspergillus oryzae* (AOL) CJLU-31 obtained from WCO soil for biodiesel synthesis. As MOFs, ZIF-8 and ZIF-L were used which were later coated with polydimethylsiloxane (PDMS) to induce hydrophobic adsorption via the CVD method for 18 h. Both the synthesized composites, PDMS-ZIF-L and PDMS-ZIF-8, were immobilized by *Aspergillus oryzae* lipase with the help of hydrophobic interaction via direct surface physical adsorption. The syntheses processes of AOL@ZIF-L and AOL@PDMS-ZIF-L are shown in Fig. 18. The specific surface areas of PDMS-ZIF-L and PDMS-ZIF-8 were obtained as 1583.22 m²/g and 160.21 m²/g respectively. The SEM images (Fig. 19) indicated that the prepared materials contained polyhedrons and cruciate flower-like morphology. This study also showed that PDMS coating modification did not affect the structural morphology of ZIF-8 and ZIF-L. The presence of Si elements on PDMS-ZIF-L and PDMS-ZIF-8 were confirmed through TEM and EDS analyses (Fig. 20), which could prove the successful modification of ZIF-L and ZIF-8 by PDMS coating. The activity recovery of the immobilized composite, AOL@PDMS-ZIF-L, was upgraded maximum to 26 fold (430%) when compared to AOL@ZIF-L which was obtained at 0.24 mg/ml lipase concentration. The synthesized catalyst, AOL@PDMS-ZIF-L, was then employed for biodiesel production using soybean oil with methanol. The ORCs for the reactions were taken as 2 wt% of AOL@PDMS-ZIF-L catalyst, and 4:1 of MTOR at 45 °C in 24 h that produced 94.37% of biodiesel. Furthermore, even after the 5th repeated cycle of reaction, the catalyst could preserve 85% biodiesel yield exhibiting good reusability.

Liu et al. (2021) immobilized *Candida antarctica* lipase B (CALB) on biobased MOF for the esterification of oleic acid with methanol to produce biodiesel. A MOF was synthesized with adenine, acting as an organic linker via biomimetic assembly and immobilization of CALB being done concomitantly resulting in a solid material, CALB@MOF. The prepared catalyst CALB@MOF was then applied in biodiesel synthesis. By employing central composite design (CCD) of RSM, the various parameters involved were examined such as catalyst loading, ATOR, temperature, and time. The actual yield of the reaction came out to be 98.9 ± 0.4% which was adjacent to the prediction value of the regress model (100%). The ORCs for the aforementioned yield were determined to be 117.77 mg of catalyst loading, 3.65:1 of MTOR,

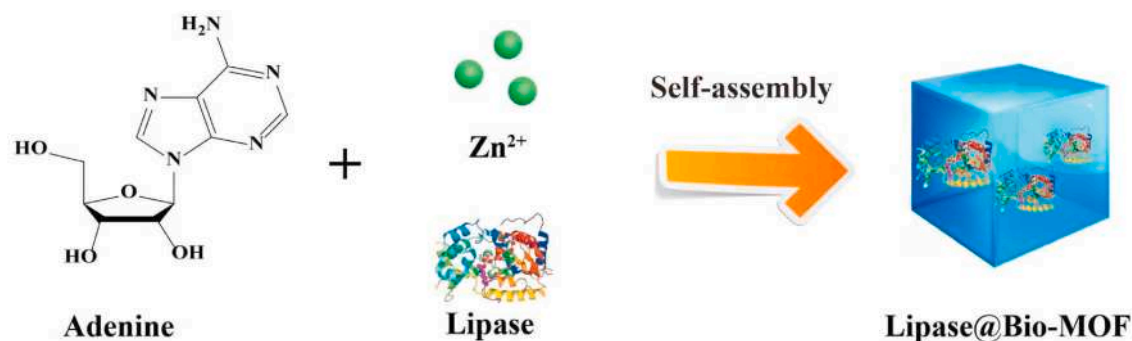


Fig. 16. Biomimetic mineralization based synthesis of lipase@Bio-MOF. Reproduced from reference (Li et al., 2020b) with permission of Elsevier, Copyright © 2020 (License no. 5263680989733).

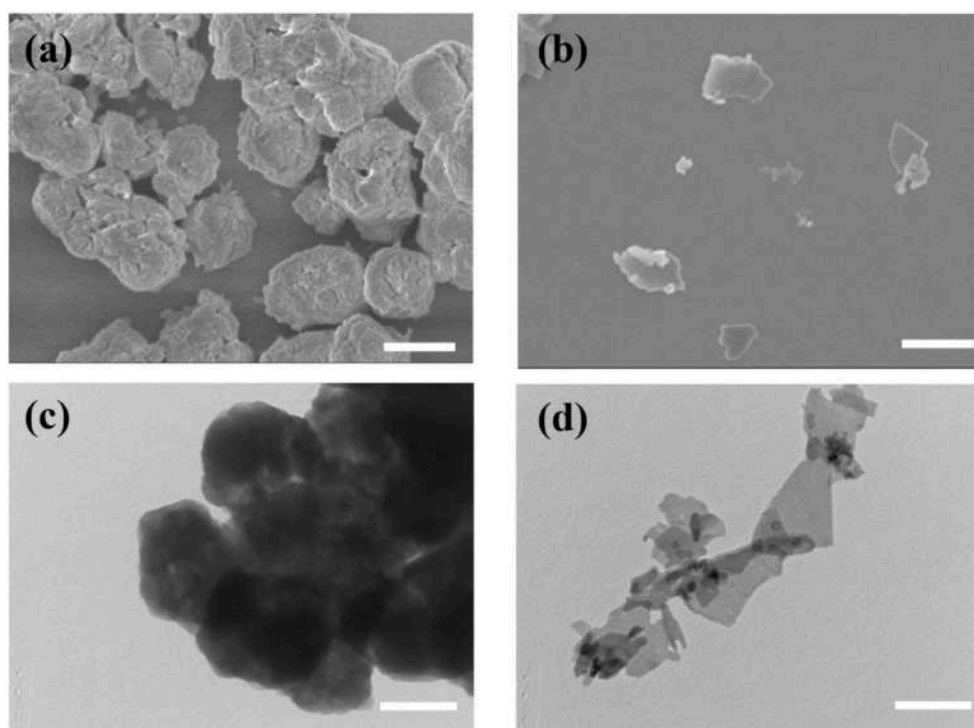


Fig. 17. SEM images (a, b) with a scale bar of 1 μm , and TEM images (c, d) with a scale bar of 500 nm of lipase@Bio-MOF (a, c) and me-Bio-MOF (b, d). Reproduced from reference (Li et al., 2020b) with permission of Elsevier, Copyright © 2020 (License no. 5263680989733).

46.3 °C of reaction temperature, and 11.55 h of reaction time.

Zhou et al. (2021) studied the enzymatic activity of biocatalyst produced by immobilization of RML onto magnetic COFs (Fe_3O_4 @COF-OMe) composite (COF-Covalent organic frameworks) in biodiesel preparation from JCO. The immobilization of RML to the prepared composite was done by physical adsorption of composite with RML dissolved in phosphate buffer saline. The prepared catalyst, RML@ Fe_3O_4 @COF-OMe, had high uptake capacity. Magnetic property analysis indicated that though Fe_3O_4 showed high magnetic property, the magnetic property of Fe_3O_4 @COF-OMe (~20 emu/g) was found to reduce after immobilization of lipase (~6 emu/g). After the immobilization of RML, the BET surface area of 232 cm^2/g (Fe_3O_4 @COF-OMe) decreased to 28 cm^2/g . The pore size of the material was found to be 3.1 nm which indicated that magnetic COF served as a promising carrier of lipase immobilization. It was found that activity of Fe_3O_4 @COF-OMe decreased after RML incorporation and could be recovered to only 60%. The catalyst showed thermal and pH stabilities. The biocomposite catalyst could produce a maximum yield of 67.8% JCO biodiesel at ORCs of 0.5 mg of catalyst amount, 0.15 mmol of oil, 0.45 mmol of methanol,

and 50 °C of temperature.

The adsorption of glycerol on immobilized lipase is a concern in lipase-mediated reactions. Hence, Hu et al. (2020b) tried to build a lipase immobilized catalyst (ANL@M-ZIF-8-PDMS; M-ZIF-macroporous ZIF) that would not be adsorbed by glycerol during biodiesel synthesis. ANL@M-ZIF-8-PDMS showed better activity recovery and performance in biodiesel synthesis than that of ANL@M-ZIF-8 material. Hydrophobic modification displayed lower glycerol adsorption, which was probably due to the improved performance of immobilized lipase in biodiesel synthesis. ANL@M-ZIF-8-PDMS showed >96% activity even after the 5th cycle of reuse.

Badoei-Dalfard et al. (2021) synthesized lipase immobilized Zr-MOF/PVP composite through the electrospinning method. The catalytic activity of immobilized enzyme enhanced due to Cu^{2+} , Co^{2+} , Mg^{2+} , Hg^{2+} and Mn^{2+} . Electrospinning enhanced the size of Zr-MOF/PVP crystals and had a very large surface area of 1928 m^2/g . Ultrasound-assisted transesterification of *R. communis* oil with methanol was carried out at 3:1 of MTOR, and 2 mg of catalyst amount that produced maximum conversion of 83% after 12 h of incubation The

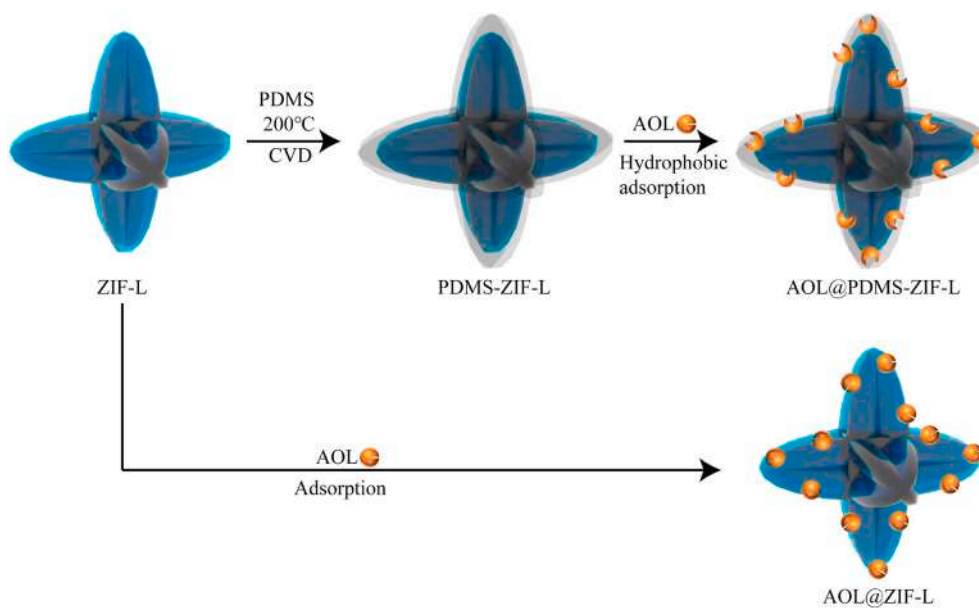


Fig. 18. Showing the synthesis process for AOL@ZIF-L and AOL@PDMS-ZIF-L. Reproduced from reference (Zhong et al., 2021) with permission of Elsevier, Copyright © 2021 (License no. 5263660595843).

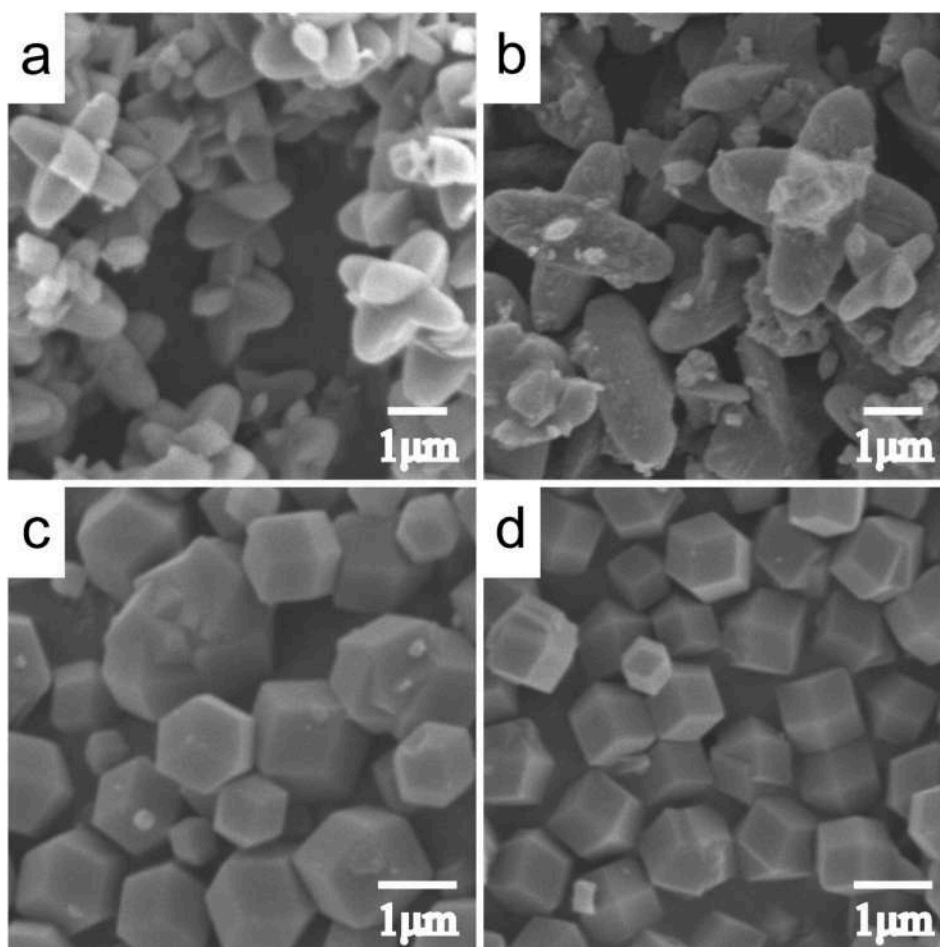


Fig. 19. SEM images of (a) ZIF-L, (b) PDMS-ZIF-L, (c) ZIF-8, and (d) PDMS-ZIF-8. Reproduced from reference (Zhong et al., 2021) with permission of Elsevier, Copyright © 2021 (License no. 5263660595843).

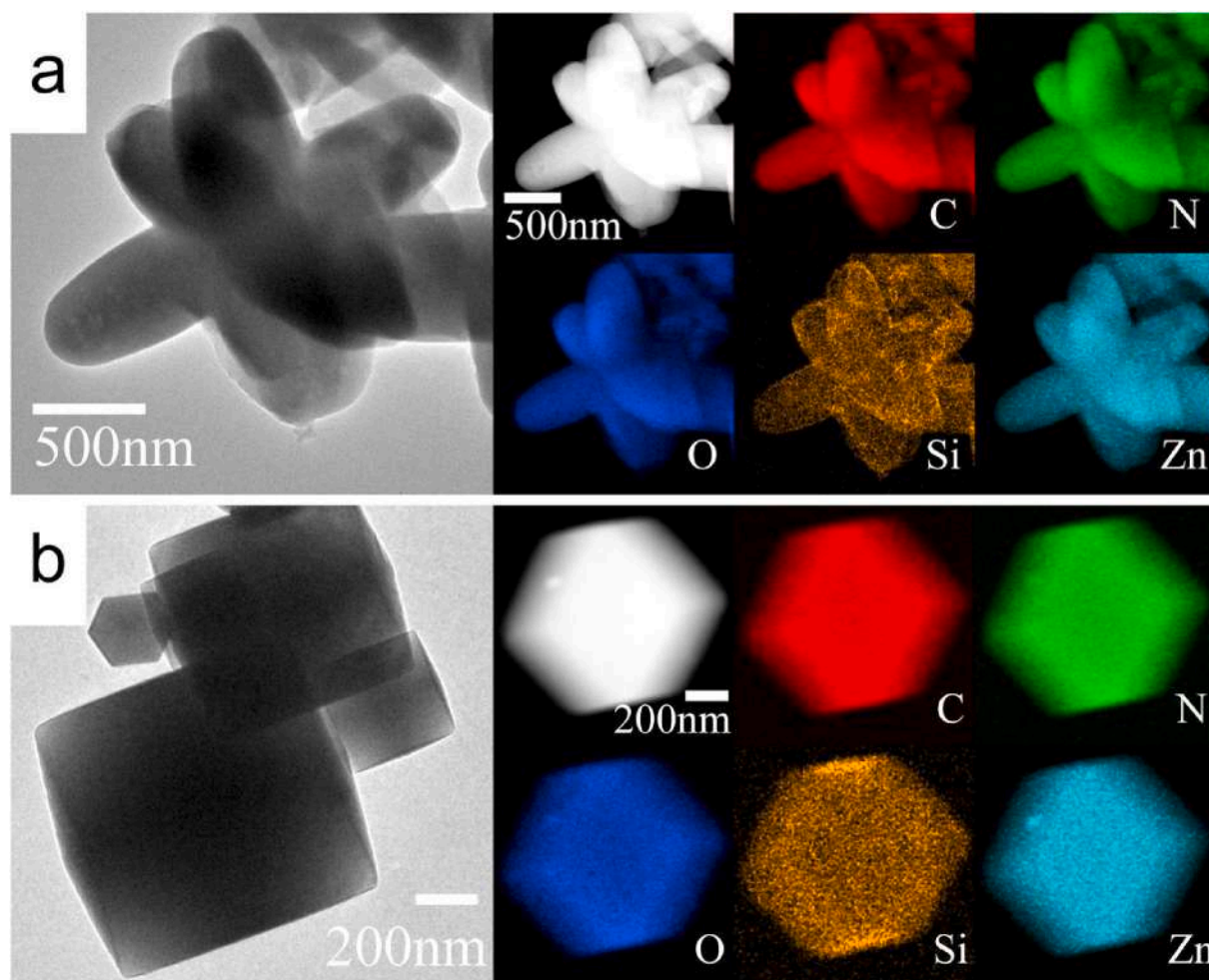


Fig. 20. TEM images and elemental mapping of (a) PDMS-ZIF-L and (b) PDMS-ZIF-8. Reproduced from reference (Zhong et al., 2021) with permission of Elsevier, Copyright © 2021 (License no. 5263660595843).

catalyst was reused up to the 7th cycle retaining 65.9% of its initial activity at the end of 7th cycle due to covalent immobilization of lipase.

Hu et al. (2021) synthesized large pore-sized MOFs which allowed a high amount of enzyme immobilization, and the developed catalyst was named ANL@M-ZIF-8. Further, the microporous catalyst was prepared via surface immobilization of ANL on ZIF-8 (ANL/ZIF-8) to compare the catalytic activity with ANL@M-ZIF-8 in the transesterification of soybean oil. At the reaction conditions of 10 g of soybean oil, 45 °C of reaction temperature, four stepwise additions of 460 μ L of methanol, and 0.1 g of ANL@M-ZIF-8, 80% of biodiesel was obtained in 24 h. However, on using 0.7 g of ANL/ZIF-8, 65% of the product was obtained in 12 h. ANL@M-ZIF-8 could be reused up to the 5th cycle while ANL/ZIF-8 could be reused only till the 2nd cycle.

Al-Mansouri et al. (2022) encapsulated soluble lipase from *Eversa transform 2.0* in hexagonal ZIF-8 (L@ZIF). The catalyst was used in the synthesis of biodiesel via transesterification of olive oil with methanol. The highest biodiesel yield was achieved under the conditions of MTOR of 6:1, reaction temperature of 40 °C and reaction time of 4 h with encapsulated lipase of 0.2 g.

Shomal et al. (2022) synthesized three catalysts viz. ZIF-67, ZIF-8 and HKUST-1. *Thermomyces lanuginosus* was immobilized on ZIF-67 and ZIF-8 by physical adsorption and HKUST-1 by chemical adsorption. The catalytic activities of the three catalysts were investigated for biodiesel synthesis from olive oil. Among the three catalysts, ZIF-8 and ZIF-67 were found to have a better catalytic activity which reported the oil conversion of 88% and 90%, respectively under the ORCs of 12:1 of MTOR, 20 wt% of catalyst dosage, 4 h of reaction time and 40 °C of

reaction temperature. Under the same conditions, HKUST-1 showed 71.8% of oil conversion.

The various studies being discussed above showed that MOF composites act as a befitting carrier for various enzyme immobilization enhancing their catalytic performances altogether. However, proper attention must be given to selecting the appropriate support material and encapsulation techniques in order to construct a qualified enzymatic catalyst.

2.4. Bifunctional based MOF catalyzed biodiesel production

The heterogeneous catalysts used in biodiesel production can be either acidic or basic. Both of these catalysts have their advantages as well as drawbacks. The applications of heterogeneous solid catalysts are restricted to a moderate amount of FFA content (Kondamudi et al., 2011). This issue can be addressed by synthesizing a catalyst that exhibits both acidic and basic sites which are referred to as bifunctional catalysts. The transesterification and esterification reactions of triglycerides and FFAs can be simultaneously carried out employing a bifunctional heterogeneous catalyst (Elias et al., 2020). Studies have shown that MOFs can play an important role in preparing bifunctional catalysts because of their high surface area, controllable structure, and tunable properties. MOFs can feasibly change their active sites by changing their ligands and functionalities and thereby act as bifunctional catalysts. MOF-derived bifunctional catalysts are green and sustainable and exhibit high catalytic activity [109]. The summarized data presented in Table 6 shows the performances of different bifunctional

Table 6
Catalytic performance of different bifunctional MOFs catalysts.

Biodiesel feedstock/ Alcohol	Catalyst	Catalyst preparation method	Biodiesel synthesis method	Surface area (m ² g ⁻¹)	Reaction conditions					Reference
					ATOR	Catalyst (wt %)	Temp (°C)	Time (h)	Product, Y or C (%)	
OA/methanol	UiO-66(Zr)-NO ₂ -green	Green method	Esterification	649	39:1	6	60	4	90.7 (Y)	Abou-Elyazed et al. (2019)
OA/methanol	UiO-66(Zr)-NH ₂ -green	Green method	Esterification	823	39:1	6	60	4	97.3 (Y)	Abou-Elyazed et al. (2019)
LA/methanol	UiO-66-NH ₂	–	Esterification	–	26:1	8	60	2	>99 (Y)	Cirujano et al. (2015)
LA/ethanol	UiO-66	–	Esterification	–	18:1	8	78	8	64 (Y)	Cirujano et al. (2015)
LA/ethanol	UiO-66-NH ₂	–	Esterification	–	18:1	8	78	8	99 (Y)	Cirujano et al. (2015)
LA/methanol	UiO-66	–	Esterification	–	26:1	8	60	2	94 (Y)	Cirujano et al. (2015)
RO/methanol	HZN-2	Solvothermal method	Transesterification	457.02	10:1	4	200	2	98.02 (C)	Jeon et al. (2019)
WCO/methanol	Cu-MOF + Ca-MOF	Solvothermal method	Transesterification and esterification	–	20:1	1	60	1	85 (Y)	Jamil et al. (2020)
<i>Chlorella vulgaris</i> /methanol	HPW/ZIF-67	–	Transesterification and esterification	1137	20:1	1	200	1.5	98.5 (C)	Cheng et al. (2021)

ATOR–Alcohol to oil ratio; Temp–temperature; C–conversion; Y–yield; h–hour; LA–Lauric acid; OA–Oleic acid; RO–Rapeseed oil.

MOF catalysts in biodiesel synthesis.

Abou-Elyazed et al. (2019) utilized a series of defected UiO-66(Zr) structured materials as heterogeneous catalysts for the esterification reaction of oleic acid. They synthesized UiO-66(Zr)-NH₂ and UiO-66(Zr)-NO₂ functionalized UiO-66(Zr) by a green method. The BET surface area of UiO-66(Zr), UiO-66(Zr)-NH₂-green and UiO-66(Zr)-NO₂-green were obtained as 1115, 823 and 649 m²/g respectively, which indicated the change in the physical properties of UiO-66(Zr) after incorporation of electron-withdrawing and electron-donating groups. The trend of acid strength was UiO-66(Zr)-NO₂-green > UiO-66(Zr)-green > UiO-66(Zr)-NH₂-green. The prepared catalysts were employed in the production of methyl ester from oleic acid using methanol. The resultant yields of biodiesel were obtained as 90.7% and 97.3% for UiO-66(Zr)-NO₂-green and UiO-66(Zr)-NH₂-green, respectively. The ORCs using both the catalysts were taken as 39:1 of MTOAR, 6 wt% of catalyst loading, and 60 °C of temperature in 4 h of reaction time. All the catalysts showed a good reusability character with more than 60% yield of FAME after three consecutive cycles.

Cirujano et al. (2015) studied the activity and stability of Zr containing MOF as a catalyst by using terephthalate (UiO-66) and 2-amino-terephthalate ligands (UiO-66-NH₂) for esterification reaction of saturated and unsaturated fatty acids (lauric acid) using short-chain alcohols like MeOH and EtOH. In the study, it was explained that the amino group in UiO-66-NH₂ could assist the activation of the nucleophilic character of the alcohol and elimination of the water molecule, thereby UiO-66-NH₂ showed higher catalytic activity. When methanol was used as a reactant using 8 mol% catalyst and 1:26 of oil to methanol ratio for both UiO-66 and UiO-66-NH₂, the catalyst needed 2 h to produce 94% and >99% yield of FAME, respectively at 60 °C. On the other hand, when ethanol was used as a reactant using 8 mol % of catalyst and 1:18 of oil to ethanol molar ratio, the reaction was completed in 8 h yielding 64% and 99% of FAME at 78 °C. It was observed for all the cases that esterification with MeOH is considerably faster than with EtOH, because of the lower activation energy of the addition step during the reaction and higher nucleophilic character of MeOH. It was found that UiO-66-NH₂ was more active than UiO-66 for esterification of lauric acid bearing a higher yield of the ester.

Jeon et al. (2019) demonstrated the application of acid-base bifunctional heterogeneous catalyst for efficient transesterification of rapeseed oil. To achieve this, they first synthesized ZIF-8 NPs using a zinc precursor and 2-methylimidazole via a solvothermal method. It had

been shown that ZIF-8 NPs were not suitable for direct use as a catalyst due to the lack of catalytic activity. Thereby, they synthesized a highly efficient catalytic hybrid material after functionalizing ZIF-8 NPs with HPA through an imidazole medium. Various ratios of HPA to ZIF-8 NPs were used for the study of catalytic efficiency referred to as HZN numbers. Series of HZN numbers such as HZN-1, 2, 3, 4 were prepared with HPA concentrations of 0.05, 0.1, 0.3, and 0.5 g, respectively. The formation of HZN between the Keggin structure in the HPA and imidazole group in the ZIF-8 NPs was indicated through strong O–N bonding. The highest conversion of 98.02% was obtained for HZN-2 at ORCs of 4 wt% of catalyst, 10:1 of MTOR at 200 °C, and 2 h reaction time. The BET surface area for HZN-2 was found to be 457.02 m²/g. Moreover, the catalyst showed good recyclability owing to sufficient surface area and strong acid bifunctionality. This study provided better insight into hybrid MOF materials synthesized through simple catalytic functionalization.

Jamil et al. (2020) studied the combination of Cu-based MOF as an acid catalyst and Ca-based MOF as a base catalyst for simultaneous esterification and transesterification. The Cu-MOF was prepared by adopting a modified solvothermal method with 1:1 M ratio of the metal salt (CuSO₄·5H₂O) and BDC. Then the Ca-MOF catalyst was synthesized by using the modified hydrothermal method with 1:1 M ratio of CaCO₃ and BDC. From XRD analysis, the average crystallite size for Cu-MOF and Ca-MOF were determined to be 49.0 nm and 20.8 nm respectively. Cu-MOF material (Fig. 21) indicated a well-defined crystal structure with rectangular sheets and 31.74% Cu content was detected. The SEM images (Fig. 22) of Ca-MOF indicated cubical shape particles having 5–7 μm sizes. The EDS spectrum (Fig. 22d) showed 33% of Ca in Ca-MOF material. The thermal stability of Cu-MOF was shown to exhibit above 400 °C, whereas that of Ca-MOF was observed until 520 °C depicted by TGA curves. The BET surface area and total pore volume of Cu-MOF were determined to be 118 m²/g and 0.087 cm³/g respectively. Moreover, the BET surface area and total pore volume for Ca-MOF were measured as 101 m²/g and 0.035 cm³/g respectively. For the combination of catalyst (Cu-MOF + Ca-MOF), the flashpoint, saponification value, iodine value, and cetane number were obtained as 130.5 °C, 247.6 mg KOH g⁻¹, 61.3 gI₂/100 g oil, and 52 respectively, which were in agreement with ASTM standard. The biodiesel synthesis from WCO with methanol was carried out using the combination of catalyst (Cu-MOF + Ca-MOF), which produced 85% yield. The ORCs were found to be 20:1 of MTOR, 1 wt% of catalyst loading, 60 °C of temperature, and

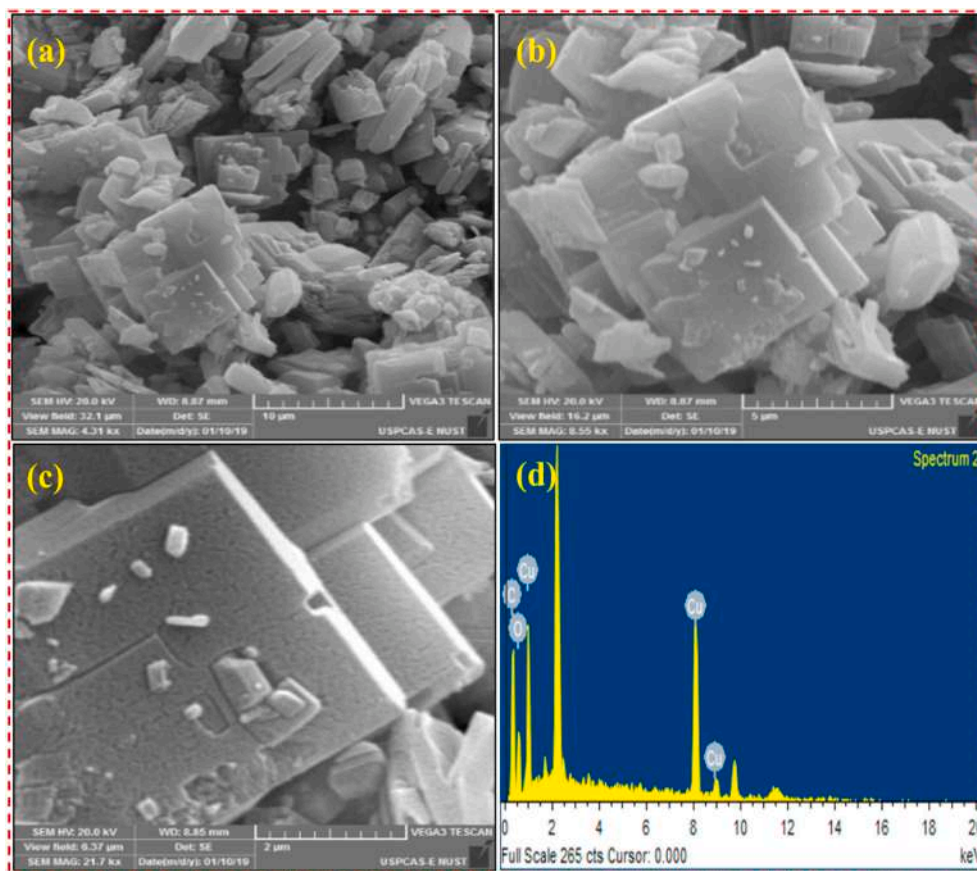


Fig. 21. SEM images of Cu-MOF material (a–10 μm, b–5 μm, c–2 μm), and (d) EDS analysis. Reproduced from reference (Jamil et al., 2020) with permission of Elsevier, Copyright © 2020 (License no. 5263690968088).

1 h of reaction time. The unsaturated open sites imparted by the catalyst combination of Cu-MOF and Ca-MOF could coordinate with triglycerides and methanol. Also, the other chemical properties such as electron delocalization, nucleophile attack, and interface dipole helped in aiding the transesterification process. The catalyst maintained 75.1% biodiesel yield at the third consecutive reaction cycle. Furthermore, after performing RSM, it was observed that the biodiesel yield was affected mainly by catalyst loading and reaction temperature, while the quality of biodiesel was influenced by the ATOR.

A bifunctional solid catalyst (acid-base) was synthesized by Cheng et al. (2021) which was carried out by modifying Co-based zeolite ZIF-67 with HPW. XPS analysis indicated that immobilization of HPW to ZIF-67 formed new N–O bonds and destroyed Co–N covalent bonds in ZIF-67. The increased amount of HPW resulted in more unsaturated Co cations and N⁻ extremities thereby increasing the Brønsted acid as well as Lewis acid, and Lewis base sites. W–O–N bond was observed and its content decreased with increasing HPW amount in ZIF-67. This was because of W–O–N bond entered into the pores of ZIF-67 as HPW could not bind ZIF-67 easily. This evidence was further confirmed by SEM analysis which showed that the crystal structure was found to disappear with the rise in HPW content. Among the different proportions of HPW/ZIF-67 catalyst, HPW/ZIF-67 with a weight ratio of 0.25 was found to show the most efficient activity due to its acid-base site distribution. Its surface area was found to be 1137 m²/g. The catalyst was applied for the esterification and transesterification of microalgal lipid (*Chlorella vulgaris*) to synthesize biodiesel. The highest conversion of 98.5% was achieved under the reaction conditions of 1 wt% of catalyst, 20:1 of MTOR, 200 °C of temperature and 90 min of reaction time. The catalyst also showed good reusability and could be reused up to the 6th cycle showing a good conversion of 91.3%.

3. Fuel properties of biodiesel obtained using MOFs catalysts

The quality of biodiesel is influenced by the source of feedstock as well as the reaction process of synthesizing the biodiesel. The transesterification process reduces the viscosity and density of the oil and in turn improves the volatility to some extent (Lee et al., 2015). Before being commercially employed, the resultant biodiesel must undergo certain characterization with the purpose to scrutinize the designations provided by ASTM-D6751 and EN-14214 standards. The several properties that need to agree with the above-mentioned standards include cetane number, flash point (°C), viscosity (mm²/s), density, specific gravity, cloud point (°C), pour point (°C), calorific value, saponification value, iodine value, etc. (Basumatary et al., 2018, 2020). The carbon number and the concentration of FAME determine the cetane number. The index of flammability of the fuel is evaluated by cetane number. For facile fuel and engine operation, a high cetane number is expected which also reduces the white smoke production. The ideal value of cetane number for biodiesel should be a minimum of 47. The flashpoint (°C) with a minimum value of 130 or higher is necessary for fire safety purposes. Usually, low viscosity is demanded better fuel combustion with the standard value of 1.9–6.0 mm² s⁻¹ for biodiesel. The value of density for petro-diesel as per ASTM-D6751 standard is 848 kg m⁻³ and that for biodiesel is around 0.88 g cm⁻³ which ensures the complete combustion of fuel. The standard specific gravity lies in the range 0.86–0.9. Usually, the low-temperature cloud point is expected for biodiesel for better performance. The pumping ability of the fuel is indicated by the pour point. Ideally, biodiesel should have a calorific value of around 37.3 MJ kg⁻¹ for good operation. The saponification value of biodiesel is associated with low yield and poor quality. The maximum estimated value of saponification of biodiesel is found to be

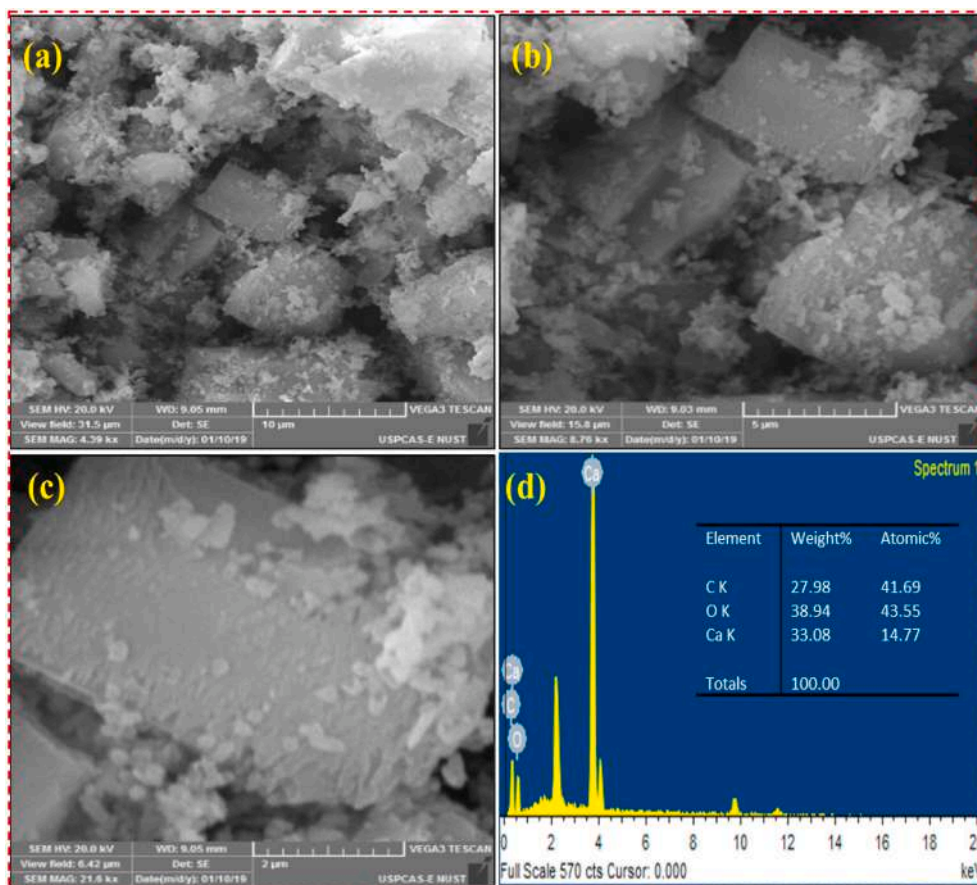


Fig. 22. SEM images of Ca-MOF material (a–10 μm , b–5 μm , c–2 μm), and (d) EDS analysis. Reproduced from reference (Jamil et al., 2020) with permission of Elsevier, Copyright © 2020 (License no. 5263690968088).

312 mg KOH g^{-1} (Jamil et al., 2020). The iodine number measures the degree of unsaturation of the resultant biodiesel. The standard iodine value is a maximum of 120 g $\text{I}_2/100$ g oil. The higher the degree of unsaturation, the higher is the chances of polymerization leading to less oil stability (Jamil et al., 2020). Table 7 displays the properties of biodiesel obtained from transesterification and esterification of oil feedstocks using different MOF-supported catalysts. The data showed indicates that the biodiesel synthesized using MOF-supported catalysts is in accordance with the standard values in all aspects. The results thus

convey that MOF derivatives can act as potential heterogeneous solid base catalysts and the biodiesel synthesized using these catalysts are suited for practical implementation.

4. Catalytic comparison between different types of MOFs-based catalysts and other catalysts used in biodiesel synthesis

In this study, catalytic activities of different MOF catalyst systems such as acidic (Table 3), basic (Table 4), enzymatic (Table 5) and

Table 7

Comparison of the properties of biodiesel produced using various MOFs catalysts.

Biodiesel feedstock/Alcohol	MOF catalyst	Density at 15 °C (g/cm ³)	Kinetic viscosity at 40 °C (mm ² /s)	Cetane number	Specific gravity	Flash point (°C)	Iodine value (g I ₂ /100 g)	Acid value (mg KOH/g)	Saponification number (mg KOH/g)	Higher heating value/Calorific value (MJ/kg)	Reference
OA/methanol	UiO-66/SFN	0.88	3.83	–	–	132	–	0.02	–	–	Li et al. (2021a)
SO/methanol	KNa/ZIF-8@GO	0.87	–	–	–	156	–	0.23	–	–	Fazaeli and Aliyan (2015)
PO/methanol	Fe@C-Sr	0.88	3.96	–	–	158	–	0.02	–	–	Li et al. (2019)
SO + SFO	NaOH/magnetized ZIF-8	0.8875	5	65	–	140	–	0.1	–	–	Abdelmigeed et al. (2021)
WCO/methanol	Cu-MOF + Ca-MOF	0.88	5.9	52	0.88	130.5	61.3	–	247.6	40.4	Jamil et al. (2020)
ASTM-D6751 Standard	–	0.87–0.9	1.9–6.0	≥47	0.86–0.9	>130	<120	–	<312	>35	Jamil et al. (2020)

Table 8

Catalytic activity of other non-MOF catalysts such as metal oxide, ionic liquid, enzyme and zeolite based catalyst used in biodiesel synthesis.

Biodiesel feedstock	Catalyst	Surface area (m ² g ⁻¹)	Reaction conditions					Reference
			ATOR	Catalyst (wt %)	Temp (°C)	Time (h)	Product (%)	
Soybean oil	Fe ₃ O ₄ /MCM-41/ECH/Na ₂ SiO ₃	54.3	25:1	3	Methanol reflux temp	8	99.2	Xie et al. (2018a)
Karanja oil	[Chol ⁺][H ₂ PO ₄ ⁻]	–	43:1	8	275	0.75	95.6	Ortiz-Martínez et al. (2016)
Oleic acid	PEI/PS-1/5 [Ionic liquid]	–	21.5:1	4.6	70	2	97.24 (C)	Lin et al. (2021)
Oleic acid	[TMPP-PS][CF ₃ SO ₃] ⁻ IL	–	12:1	4	70	3	92.91 (C)	Chen et al. (2020)
Chicken fat	CaO/CuFe ₂ O ₄	–	15:1	3	70	4	94.52	Seffati et al. (2019)
Sunflower oil	MgO-La ₂ O ₃	151.7	18:1	3	65	5	97.7	Feyzi et al. (2017)
WCO	MgO-NaOH	–	6:1	3	50	6	98	Rafati et al. (2019)
JCO	Lipase-PDA-TiO ₂	–	6:1	10	37	30	92	Zulfiqar et al. (2021)
JCO	SO ₄ ²⁻ /TiO ₂	80.9	9:1	4	140	24	85.3	Chen et al. (2018)
Sunflower oil	Ca/Fe ₃ O ₄ @SiO ₂	189.2	15:1	8	65	5	97	Feyzi and Norouzi (2016)
WCO	Bifunctional magnetic nano-catalyst (RHC/K ₂ O-20%/Ni-5%)	49.9	12:1	4	65	2	98.2	Hazmi et al. (2021)
WCO	Cerium-doped MCM-41	1200	9:1	5	70	6	94.3	Dehghani and Haghghi (2019)
WCO	ZnCuO/N-doped graphene	228.8	15:1	10	180	8	97.1	Kuniyil et al. (2021)
Sunflower oil	Waste chalk/CoFe ₂ O ₄ /K ₂ CO ₃	5.839	15:2	2.65	80	2.95	99.27	Foroutan et al. (2022)

bifunctional (Table 6) MOF catalysts are summarized. The catalytic activities of other non-MOF catalysts are also listed in Table 8 for comparison with MOF catalysts. Several factors influence the yield of biodiesel which include catalyst loading, ATOR, reaction time and temperature. The utilization of different support materials and synthesis methods to generate the catalyst are also important and could produce different yields of biodiesel (Aderibigbe et al., 2020). The MOF catalyst and biodiesel syntheses processes and the reactors used are also important factors in terms of efficiency and overall production cost. Different MOF catalyst systems can be prepared after post-synthetic modifications of the structure of MOF by encapsulating, immobilizing, post-functionalization and several chemical interactions.

It can be observed from Table 3 that many acidic MOFs catalysts have been developed and reported for the synthesis of biodiesel. In the process, most of the feedstocks used are the FFAs and oils with high FFA contents. The acid catalysts not only assist transesterification but also do esterification of FFAs. It is seen that most of the acidic MOFs catalyzed synthesis of biodiesel needed higher reaction temperatures, more ATOR and a large amount of catalyst. However, its reaction time needed varies from medium to large. Due to these harsh conditions, acidic MOFs catalyst may not be suitable for the commercial production of biodiesel.

Table 4 shows that the number of basic MOFs catalysts reported so far for biodiesel research is lower compared to acidic MOFs. This indicates that the research on basic MOF catalysts including bifunctional MOF catalysts (Table 6) for biodiesel synthesis is still in the nascent stage. It is seen from Table 4 that lower catalyst concentration and reaction time are needed if basic MOFs are applied. The reaction temperature and ATOR required are moderate. The reaction could produce high yields under mild conditions (Table 4) except the two catalysts, Zr-fumarate-MOF (Shaik et al., 2022) and 20MgO@Zn-MOF-370 (Yang et al., 2022). Basic MOF catalysts have comparable catalytic activities to common heterogeneous base catalysts. Due to the high efficacy and mild conditions of production processes, the base MOF catalyst has more scope for industrial application. Considering the scope for industrial perspectives, more basic MOF catalysts with higher stability could be developed using suitable metal clusters and ligands. The MOFs could be uniformly dispersed. They have a large surface area and superior catalyst structures. Moreover, the calcination process is not required if the material is synthesized via encapsulation or chemical bonding. MOF preparation employing the solvothermal method has disadvantages as the process requires a high temperature and a longer time. The adulteration of biodiesel by the leaching of active sites of the catalyst hinders its potential (Ma et al., 2021). The leaching not only pollutes the

biodiesel but also reduces the reusability of that catalyst. This should be considered for the development of a potential catalyst with strong stability.

The biodiesel production process using enzymatic catalysts is an eco-friendly and non-toxic process. However, direct use of enzymes should be avoided as they are associated with the risk of denaturation and high sensitivity to alcohol. This can be overcome by immobilizing enzymes having active sites onto the porous support with a large surface area such as MOFs. The common techniques employed for the immobilization of enzymes on MOFs are encapsulation, adsorption, and covalent bonding. Among the immobilization techniques, a better strategy for lessening the leaching of active constituents, better protection from degradation, and better reusability character were observed in the case of *in-situ* encapsulation. Rafiei et al. (2018) employed *in-situ* encapsulation to synthesize a stable and economically efficient heterogeneous biocatalyst. Enzyme immobilization using physical adsorption or covalent attachment has limitations such as leaching out of enzyme due to weak interactions with solid support and consideration of specific sizes of the enzyme to encapsulate into the space of MOF. Although enzymatic MOFs require low reaction temperature, lower ATOR, and medium catalyst concentration (Table 5), they require a longer reaction time and the biodiesel yields reported are not satisfactory. Biodiesel synthesis using enzymatic MOFs catalysts remains the major setback due to the inherently high cost and weak stability of the catalyst. However, the development of enzymatic MOFs catalysts is an important area of future research that has the prospect for eco-friendly synthesis of biodiesel. New enzyme MOFs-based materials could be explored with the introduction of more functional groups, metal cations, non-structural ligands, and multiple unsaturated metal sites. Enzyme-based MOFs with strong efficacy and enhanced stability need to be developed further.

Bifunctional MOF catalysts have both basic and acidic sites and can assist simultaneous transesterification and esterification reactions. These catalysts can resolve the shortcomings of acid-catalyzed reactions that require high temperatures. The overall reaction condition using bifunctional MOF catalysts is moderate with biodiesel yield ranging from medium to high (Table 6). However, the stability of the catalyst is weak. The utilization of bifunctional MOF catalysts (Table 6) in biodiesel synthesis is still in the infant stage and scopes are open for more deep research and development in the future. Further, the development of magnetic MOF bifunctional composites with nano-size structures will be one of the potential areas of biodiesel research for efficient activity and easy recovery and separation process.

The reusability of a heterogeneous catalyst is one of the notable

Table 9
Reusability of different MOF based catalysts studied in biodiesel synthesis.

MOF-based catalysts	Initial catalyst preparation conditions	Catalyst regeneration conditions	Product reported in each cycle (%)										Reference	
			C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10		
[SO ₃ H-(CH ₂) ₃ -HIM] ₃ PW ₁₂ O ₄₀ @MIL-100	130 °C for 72 h, 130 °C for 72 h	Centrifuged	>90	>90	<90	<90	<90	<90	<90	-	-	-	-	Wan et al. (2014)
MIL-101(Cr)-SO ₃ H	180 °C, 6 d	Hot filtration	>80	>80	-	-	-	-	-	-	-	-	-	Hasan et al. (2015)
DAIL-Fe ₃ O ₄ @NH ₂ -MIL-88B(Fe)	110 °C, 24 h	Applied magnet	>90	>90	<90	<90	<90	<90	<90	-	-	-	-	Wu et al. (2016)
PTA@MIL-53 (Fe)	Room temperature (RT)	Centrifuged	>90	>90	>90	>90	>90	<90	<90	<90	-	-	-	Nikseresht et al. (2017)
PTA@MIL-53 (Fe)	RT	Centrifuged	>90	>90	>90	-90	<90	<90	<90	-	-	-	-	Nikseresht et al. (2017)
AILs/HPW/Uio-66-2COOH	100 °C for 12 h	Filtration	>90	>90	-90	>80	80	-	-	-	-	-	-	Xie and Wan (2019d)
AILs/Uio-66-2COOH	100 °C for 12 h	Filtration	>90	-70	>50	>20	>10	-	-	-	-	-	-	Xie and Wan (2019d)
CuBTC-MOF	110 °C, 18 h	Washed with hexane	86	-	-	-	-	-	-	-	-	-	-	Pangestu et al. (2019)
Sn _{1.5} PW/Cu-BTC-1	120 °C, 6 h	Centrifuged	>80	>80	>80	>70	>70	>70	>60	-	-	-	-	Zhang et al. (2020c)
Mg ₃ (BDC) ₃ (H ₂ O) ₂	Microwave oven, 300 W, 3 h	-	>90	>90	>90	>90	<90	-	-	-	-	-	-	AbdelSalam et al. (2020)
MF-SO ₃ H	60 °C for 1 h, 120 °C, 160 °C, 200 °C	Centrifuged	>90	>90	>90	>80	>80	>70	>50	-	-	-	-	Liu et al. (2020)
NiHSiW/Uio-66	120 °C, 6 h	Centrifuged	>80	>80	>60	>60	-60	>50	>50	-50	-	-	-	Zhang et al. (2020b)
UiO-66/SFN	120 °C for 24 h	120 °C, 10 h	>90	>80	>70	>60	66.3	-	-	-	-	-	-	Li et al. (2021a)
PW-TiO ₂	150 °C, 6 h	Centrifuged	90.5	>80	>70	>70	>70	74.8	-	-	-	-	-	Zhang et al. (2021c)
PSH/Uio-66-NO ₂	120 °C for 24 h, 90 °C for 24 h	Washed with methanol	>90	<90	77.1	>60	>60	-	-	-	-	-	-	Dai et al. (2021)
Zn ₃ (BTC) ₂	85 °C for 24 h	-	>60	>60	>60	>60	>60	-	-	-	-	-	-	Lunardi et al. (2021)
HPW@CoCeO	150 °C, calcined at 350 °C for 3 h	Centrifuged	67.2	>60	>60	>60	<60	>60	>60	61.8	-	-	-	Zhang et al. (2021d)
PW ₁₂ @Uio-66	Stirred for 30 min	Centrifuged	>90	>90	>90	>90	>90	>90	>90	>90	>90	>90	>90	Zhang et al. (2021f)
HPMo/Ni-MOF	150 °C, 6 h	Centrifuged	82.4	>80	>80	>80	>80	>80	>75	>75	>74	73.5	-	Zhang et al. (2021b)
PMA/Fe-BTC	120 °C, 6 h	No treatment	>70	>70	>65	>65	>60	59.2	-	-	-	-	-	Zhang et al. (2019a)
HSiW@ZrO ₂	120 °C, 6 h	Centrifuged	94.0	>90	>90	>90	>90	>90	>90	-90	82.6	-	-	Zhang et al. (2021a)
HSiW-Uio-66	120 °C, 6 h	Centrifuged	80.5	>70	>75	>75	>70	70.2	-	-	-	-	-	Zhang et al. (2020b)
Ag ₁ (NH ₄) ₂ PW ₁₂ O ₄₀ /Uio-66.	120 °C, 6 h	Centrifuged	>70	>70	>70	>70	>60	54.6	-	-	-	-	-	Zhang et al. (2020d)
HPMo/Cu-BTC	120 °C, 6 h	Centrifuged	>90	>90	>90	>90	>80	>80	>80	-	-	-	-	Zhang et al. (2021e)
ZrSiW/Fe-BTC	70 °C for 3 h, 120 °C for 6 h	Centrifuged	>85	>80	>85	>85	>80	79	-	-	-	-	-	Zhang et al. (2020a)
ZrSiW/Uio-66	70 °C for 3 h, 120 °C for 6 h	Centrifuged	>95	>95	>95	>90	>85	88.9	-	-	-	-	-	Zhang et al. (2020a)
Zr-fumarate-MOF (MOF-801)	Stirred for 30 min	-	>60	-60	<60	-	-	-	-	-	-	-	-	Shaik et al. (2022)
UiO-G	120 °C for 24 h, 200 °C for 4 h	120 °C, 10 h	91.3	>80	76.7	66.6	-	-	-	-	-	-	-	Li et al. (2021a)
MOF-5	150 °C, 4 h	110 °C, 24 h	82.0	41.2	20.3	20.2	-	-	-	-	-	-	-	Ben-Youssef et al. (2021)
AIL/HPMo/MIL-100(Fe)	130 °C for 72 h	80 °C, overnight	95.8	93.2	92.3	91.2	90.3	-	-	-	-	-	-	Xie and Wan (2019b)
[(CH ₂ COOH) ₂ IM]HSO ₄ @H-Uio-66	90 °C for 3 h, 120 °C for 24 h, 100 °C for 7 h, 80 °C for 5 h	Centrifuged	93.82	92.6	92.7	91.5	90.9	-	-	-	-	-	-	Ye et al. (2019)
Zr-MOF/PVP	-	Washed with distilled water	-100	-100	>90	>90	>80	>70	65.9	-	-	-	-	Badoei-Dalfard et al. (2021)
20MgO@Zn-MOF-370	Calcined in air	-	>67.7	68.4	67.7	-	-	-	-	-	-	-	-	Yang et al. (2022)
H ₆ PV ₃ MoW ₈ O ₄₀ /Fe ₃ O ₄ /ZIF-8	75 °C for 3 h, Ultrasonication for 1 h	80 °C, 12 h	>80	>70	>70	>70	>70	-	-	-	-	-	-	Xie et al. (2021)
UCN650	Stirred for 1 h	Centrifuged	96.99	>80	92.76	-	-	-	-	-	-	-	-	Li et al. (2022)
UCA700	Stirred for 1 h	Centrifuged	92.94	>80	90.54	-	-	-	-	-	-	-	-	Li et al. (2022)
H ₄ SiW/MIL-100(Fe)	Stirred at RT, 1 h	Centrifuged	-80	>60	>60	>60	>60	>60	>60	>60	>60	>60	>60 (C-11)	Zhang et al. (2020e)
HPW/ZIF-67	Stirred at 27 °C, 4 h	Washed with hexane and methanol	>90	>90	>90	>90	>90	91.6	-	-	-	-	-	Cheng et al. (2021)
IRMOF-10-ED	Stirred for 24 h	50 °C, 4 h	57.6	54.1	49.3	36.6	-	-	-	-	-	-	-	Chen et al. (2014)
KNa/ZIF-8@GO	140 °C	100 °C, 600 °C	>90	>90	<90	-	-	-	-	-	-	-	-	Fazaeli and Aliyan (2015)
Fe ₃ O ₄ @HKUST-1-ABILs	200 °C, 8 h	80 °C, overnight	>80	>80	>80	>80	>80	-	-	-	-	-	-	Xie and Wan (2018b)
ZIF-90-Gua	100 °C, 18 h	80 °C	>80	>80	>80	>80	-80	-	-	-	-	-	-	Xie and Wan (2019c)
MM-SrO	160 °C, 15 h	Filtered	96.19	88.5	>80	59.91	-	-	-	-	-	-	-	Li et al. (2019)
Fe@C-Sr	600 °C, 1 h	Recovered by magnet	>90	>90	>80	80.6	-	-	-	-	-	-	-	Li et al. (2020b)

(continued on next page)

Table 9 (continued)

MOF-based catalysts	Initial catalyst preparation conditions	Catalyst regeneration conditions	Product reported in each cycle (%)										Reference		
			C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10			
NaOH/Magnetized ZIF-8	NaOH-loaded magnetized ZIF-8 MOF	200 °C, 4 h	>90	>90	–	–	–	–	–	–	–	–	–	–	Abdelmigeed et al. (2021)
BCL@cMIL-100(AI)-600	200 °C for 30 min, 600–900 °C	–	72.6	–	–	–	–	66.3	–	–	–	–	–	–	Liu et al. (2017)
BCL@cMIL-100(AI)-800	200 °C for 30 min, 600–900 °C	–	80.3	–	–	–	–	43.3	–	–	–	–	–	–	Liu et al. (2017)
Lipase@ZIF-67	Stirred at 25 °C, 60 min	Centrifuged	>70	>70	>60	>60	>60	>60	58.7	–	–	–	–	–	Rafiei et al. (2018)
BCL-ZIF-8	Stirred, 200 rpm, 30 °C, 20 min	–	>90	>90	>80	>80	>70	>70	>70	>70	>70	–	–	–	Adnan et al. (2018a)
ANL/UiO-66-PDMS-6	Stirred (300 rpm) at RT	Centrifuged	>90	>90	>90	>90	>90	>90	<90	<90	<90	<90	83.0	–	Hu et al. (2018)
RML@ZIF-8	Stirred at 200 rpm, 30 °C for 20 min	–	>95	>90	>90	>90	>90	>90	>90	>90	<90	<90	84.7	–	Adnan et al. (2018b)
Lipase-Fe ₃ O ₄ @MIL-100(Fe)	–	Washed with phosphate buffer solution	>90	>90	>80	>80	>80	84	–	–	–	–	–	–	Xie and Huang (2019a)
Lipase@Bio-MOF	Incubation at RT for 48 h	Filtration	>80	>70	>70	>60	>60	–	–	–	–	–	–	–	Li et al. (2020b)
AOL@PDMS-ZIF-L	200 °C, 18 h	Centrifuged	>90	>90	>85	>85	85	–	–	–	–	–	–	–	Zhong et al. (2021)
ANL@M-ZIF-8-PDMS-2h	75 °C for 30 min, 200 °C for 6 h	Centrifuged	>100	>98	>97	>96	>96	–	–	–	–	–	–	–	Hu et al. (2020b)
ANL@M-ZIF-8-PDMS-6h	75 °C for 30 min, 200 °C for 6 h	Centrifuged	>100	>100	>98	>96	>96	–	–	–	–	–	–	–	Hu et al. (2020b)
ANL@M-ZIF-8-PDMS-10h	75 °C for 30 min, 200 °C for 6 h	Centrifuged	>100	>100	>98	>96	>96	–	–	–	–	–	–	–	Hu et al. (2020b)
UiO-66(Zr)-NO ₂ -green	130 °C, 150 °C for 12 h	100 °C, 150 °C, 6 h	>90	>70	>70	–	–	–	–	–	–	–	–	–	Abou-Elyazed et al. (2019)
UiO-66(Zr)-NH ₂ -green	130 °C, 150 °C for 12 h	100 °C, 150 °C, 6 h	>90	>70	>50	–	–	–	–	–	–	–	–	–	Abou-Elyazed et al. (2019)
HZN-2	Stirred at RT for 1 h	Dried	>50	>50	>50	>50	>50	–	–	–	–	–	–	–	Jeon et al. (2019)
Cu-MOF + Ca-MOF	85 °C for 24 h, 110 °C for 48 h	110 °C	80.2	78	75.1	–	–	–	–	–	–	–	–	–	Jamil et al. (2020)
Encapsulated L-ZIF	–	Centrifuged	100	>60	>60	>60	–	–	–	–	–	–	–	–	Al-Mansouri et al. (2022)
ANL@M-ZIF-8	Reacted for 24 h at 75 °C (450 rpm)	Centrifuged	100	>90	>80	>70	68	–	–	–	–	–	–	–	Hu et al. (2021)
Adsorbed L-HKUST-1	120 °C	Centrifuged	>70	>60	>50	>20	–	–	–	–	–	–	–	–	Shomal et al. (2022)
Encapsulated L-ZIF-8	100 °C	Centrifuged	100	>70	>50	>10	–	–	–	–	–	–	–	–	Shomal et al. (2022)
Encapsulated L-ZIF-67	100 °C	Centrifuged	100	>80	>30	>20	–	–	–	–	–	–	–	–	Shomal et al. (2022)

benefits in the synthesis of biodiesel, which significantly reduces the production cost. The deactivation of a catalyst may arise due to the leaching of active sites of the catalyst, poisoning of active sites, coverage of active sites, overlapping of active sites, and deformation of structures (Ma et al., 2021). The reusability studies of different MOFs-based catalysts in several cycles of biodiesel synthesis are summarized in Table 9. The stabilities of MOFs catalysts such as PW₁₂@UO-66 (Zhang et al., 2021f), HPMo/Ni-MOF (Zhang et al., 2021b), HSiW@ZrO₂ (Zhang et al., 2021a), H₄SiW/MIL-100(Fe) (Zhang et al., 2020e), ANL/UO-66-PDMS-6 (Hu et al., 2018), and RML@ZIF-8 (Adnan et al., 2018b) are relatively better than other MOFs catalysts mentioned in Table 9. MOFs can be employed as efficient and stable catalysts due to their large surface area, modifiable functional groups, uniform structure, and tunable pore size. The active sites of MOFs can be dispersed completely on their surface enhancing the availability of active sites and improving the reusability capacity. The tunable pore size and uniform structures of MOFs catalysts can prevent the leaching of active sites (Ma et al., 2021).

It can be observed from Table 8 that the catalytic activities and reaction conditions of some other non-MOF catalysts listed are comparable to that of basic MOFs (Table 4) and bifunctional MOFs (Table 6) catalysts. However, MOFs-based materials have better stability and are found to be more appropriate for supporting the metallic oxides of acid/alkaline (Ma et al., 2021). Basic MOFs and bifunctional MOFs catalysts are also suitable catalysts for biodiesel synthesis at the industrial scale. One advantage of bifunctional MOF catalyst is that it can save the calcination process and its reaction conditions are milder. Due to larger surface area, adaptable functional groups, uniform structure, and tunable pore size, the MOFs have more scopes for the development of efficient and cost-effective catalysts in the future.

The error and uncertainty analyses of different MOF catalysts (Tables 3–6) and other catalysts (OC) reported (Table 8) are represented in Fig. 23. The average of the several data reported was considered for analysis. The main parameters considered were the biodiesel yield (%),

catalyst load (wt.%), temperature (°C), and time (h). The 5% error bar (Fig. 23) of the average yield reported showed non-significant differences in the usage of different catalysts. Tobío-Pérez et al. (2021) also reported error bars (5%) with a non-significant difference in the performances of different biomass-based catalysts concerning biodiesel yield. Among the different types of MOF catalysts, bifunctional MOF showed decent performance in the yield of biodiesel, whereas acidic and basic MOF catalysts showed similar performance in biodiesel yield (Fig. 23). Enzymatic MOF catalyst possesses a little more uncertainty that can be observed from Fig. 23 and comparatively lower biodiesel yield is noticed. The analysis also revealed the non-significant difference in the reliability of basic MOF, acidic MOF, and bifunctional MOF catalysts concerning the yield of biodiesel. The loading of catalyst is a significant parameter of optimization and the error and uncertainty analyses of the MOF catalysts showed comparable reliability in catalyst loading in the process of biodiesel synthesis. Fig. 23 exhibited the higher performance with minimum catalysts loading and comparatively higher reliability of bifunctional MOF catalysts among other types of MOF catalysts. Concerning the uncertainty in the yield (%), enzymatic MOF also showed more uncertainty with higher catalyst loading. Basic MOF catalyst with lower catalyst loading (wt.%) is performing well with a little higher reliability than acidic MOF catalyst. Temperature plays a significant role in the activity and speed of biodiesel conversion and the error bar indicated a comparable variation in reliability in all the MOF catalysts. Acidic MOF is performing efficiently at higher temperatures with more uncertainty than other MOF catalysts. Basic and bifunctional MOF catalysts showed similar reaction temperatures with alike uncertainty. Enzymatic MOF demonstrated significant reliability at lower reaction temperatures but simultaneously needed higher catalyst loading with lower biodiesel yield. In terms of reaction time, basic and bifunctional MOF catalysts are found to be performing well with significant reliability. Except for enzymatic MOF, the error bars of acidic, basic, and bifunctional MOF catalysts revealed non-significant differences in the reliability for biodiesel synthesis with a comparable reaction

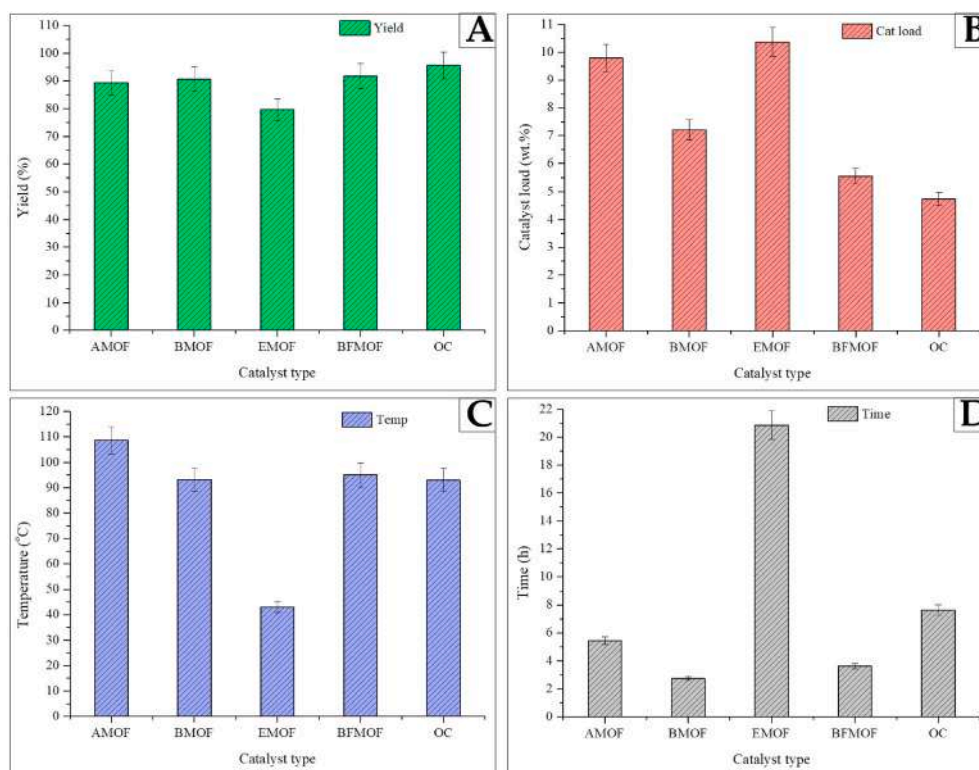


Fig. 23. Error and uncertainty analysis of acidic MOFs (AMOF), basic MOFs (BMOF), enzymatic MOFs (EMOF), bifunctional MOFs (BMOF) catalysts and other catalysts (OC) in biodiesel synthesis with respect to (A) yield (%), (B) catalyst load (wt.%), (C) temperature (°C) and (D) reaction time (h).

time. In the comparison of uncertainties concerning the yield, catalyst loading, and reaction time, the bifunctional MOF is performing well than acidic, basic, and enzymatic MOFs catalysts (Fig. 23). Though uncertainty in temperature is observed in the case of bifunctional MOF, it is indifferent to acidic and basic MOFs. The usage of other catalysts (Table 8) in biodiesel synthesis is found to be performing well, but uncertainty in temperature and higher uncertainty in reaction time is observed compared to MOF catalysts. Comparable reliability in the yield and catalyst loading is observed in the case of other catalysts (Fig. 23).

5. Production cost of biodiesel from various oil feedstocks and economic feasibility of MOFs catalysts

Biodiesel can be regarded as a renewable fuel alternative to conventional diesel fuel synthesized from materials possessing fatty acids. Some of the desirable feedstocks used in biodiesel production processes include edible and non-edible vegetable oils, animal fats, a variety of wastes containing fatty acids, and oils from microalgae. The deciding factors for the selection of feedstocks are the characteristics of fuel after modification, abundance, price, incentives, and aid from the government. Although the US and Europe were the top leading producers of biodiesel, many countries from the Middle East and South-East Asia have come forward and taken initiatives to establish biodiesel production firms, and have contributed to sophisticated technologies and advanced research needed (Barnwal and Sharma, 2005).

The production cost of biodiesel generally depends on the price of raw materials that include oil feedstocks, chemicals such as alcohols, catalysts, drying agents, reactors, the overall cost during production processes, and energy requirements. Various edible or cooking oils that are eligible as feedstocks in biodiesel production are palm oil, soybean oil, rapeseed oil, coconut oil, canola oil, corn oil, and so on. It has been noted that palm can produce the highest amount of oil out of the many aforementioned crops. Several countries with the highest production of these oils have the convenience to utilize them for the production of biodiesel. The US produces the most amount of soybean oil, rapeseed oil is produced chiefly in European countries, and Indonesia and Malaysia are the largest producers of palm oil. However, the restraint on their values can be observed owing to the competition of prices between the food and the oil which ultimately lead to a surge in prices of biodiesel. This drawback can be abolished when the oil feedstocks are easily available which can lead to the large-scale production of biodiesel. Moreover, this issue can also be resolved by using WCOs of palm, canola, corn, soybean, sunflower, etc. as they are easily available from households, restaurants, and fast food exits. Because of the high availability and low cost, these can make the biodiesel production process cost-effective which in turn reduces the production cost (Acevedo et al., 2015; Rezanian et al., 2019). Although edible oils are superior sources for biodiesel production, certain non-edible oils can be considered as suitable feedstocks. Several notable non-edible oils include JCO, rubber oil, macaw oil, yellow oleander oil, karanja oil, and so on. JCO and karanja oil are primarily produced in India and other parts of Southeast Asia, while macaw trees are native to tropical America. JCO has come to be one of the most commercially feasible alternatives to edible oils for biodiesel synthesis which has approximately 50% oil content (Koh and Ghazi, 2011). The oil content of karanja is around 30–40% which can be easily grown alongside roads and canals (Koh and Ghazi, 2011). Yellow oleander seed contains 60–65% oil, which can be planted on road-dividers and roadsides in the expressways for environmental protection, beautification, and biodiesel synthesis, which is also a potent feedstock (Deka and Basumatary, 2011). Some of the factors affecting the cost of biodiesel produced from non-edible oils include labor and operation cost, location, raw materials, and maintenance (Fadhil et al., 2017; Rezanian et al., 2019). The other suitable feedstocks besides vegetable oils are WCO, microalgae oil, sewage sludge and waste animal oils or fats. These wastes can be collected from animal slaughterhouses, food processing units, and rendering processes where animal fats or skin

such as pork lard, beef tallow, chicken fat, waste fish oil, mutton fat, etc. are usually disposed of as they are not good for human consumption. Since they contain an adequate amount of saturated fatty acids, these are desirable feedstocks for biodiesel production. Utilizing these in biodiesel production processes is a good way to convert waste to energy with the added benefit of being environmentally friendly. Beef tallow is the second leading raw material for biodiesel production in Brazil which generally possesses a low amount of sulfur and thus makes it highly desirable. The biodiesel derived from these animal waste oils attain a high yield and exhibit excellent fuel properties. Among many other animal wastes, chicken fat is given high preference because of its availability and low price (Rao and Ramakrishna, 2015; Kirubakaran and Selvan, 2018; Rezanian et al., 2019). Barnwal and Sharma (2005) in their report depicted that the primary contribution of production cost is from the cost of oil feedstock. Table 10 shows biodiesel production costs obtained from various oil feedstocks using different catalysts. This reveals the variability of biodiesel production cost due to the variation of feedstock cost in different countries. Karmee et al. (2015) demonstrated the cost varies with the catalyst that reflected the high cost of the enzyme (1047.97 USD/t) catalyzed biodiesel production from WCO compared to homogeneous acid (750.38 USD/t) and base (868.60 USD/t) catalyzed processes. Heterogeneous catalysts are preferred in terms of efficiency and reusability of catalysts in the reduction of biodiesel production cost. Naveenkumar and Baskar (2020, 2021) investigated biodiesel production cost using Zn–CaO as the heterogeneous catalyst and reported the production cost of 0.68 USD/kg for *Calophyllum inophyllum* biodiesel and 0.77 USD/kg for castor biodiesel. Ben-Youssef et al. (2021) applied MOF-5 catalyst and analyzed the biodiesel production cost from WCO and JCO and reported it to be 0.738 USD/kg and 2.385 USD/kg, respectively. The higher cost of JCO biodiesel was due to the higher cost of feedstock (Ben-Youssef et al., 2021). The cost of WCO biodiesel (0.738 USD/kg) obtained using MOF-5 catalyst was slightly lower compared to the cost of castor biodiesel (0.77 USD/kg) produced employing Zn–CaO catalyst (Naveenkumar and Baskar, 2021). This demonstrates that the MOF catalyst has the potential in terms of the cost of biodiesel. Lunardi et al. (2021) investigated the production cost of a MOF catalyst, $Zn_3(BTC)_2$, and found it to be USD 50.2/kg, which is attractive economically compared to ion-exchange resin acidic catalysts, such as Amberlyst 36 (~USD120/kg), Amberlyst 15 (~USD100/kg), and Purolite (~USD120/kg). Due to their excellent properties like good stability and reusability, MOFs are being used as potential catalysts in biodiesel synthesis. The efficient catalytic activity of MOF catalysts have been reported even after the reusability of tenth times (Adnan et al., 2018b; Hu et al., 2018; Zhang et al., 2021f), eight times (Rafiei et al., 2018), sixth times (Wan et al., 2014; Nikseresht et al., 2017), and fifth times (Xie and Wan, 2019d; Lunardi et al., 2021) (Table 9). In this way, the multiple recyclabilities of MOF catalysts will also reduce the overall biodiesel cost. Though the production cost of biodiesel obtained from certain MOF catalysts is higher compared to metal oxide catalysts (MgO and CaO), the utilization of low-quality, cheaper or waste oil feedstocks may lead to the production of lower-cost biodiesel (Lunardi et al., 2021). The biodiesel reaction process can also be improved by adopting microwave or ultrasonic-assisted technologies in place of conventional heating and stirring methods, which consume less energy and induce uniform reaction conditions leading to very less process time. The recovery of the catalysts can be further enhanced by synthesizing magnetic nano-composites making the separation process effortless. Subsidies must be provided to biodiesel production plants and industries to compete economically with conventional fuels. Considering the distinctive qualities possessed by MOF catalysts, we can say that biodiesel production utilizing these catalysts with the help of easily available feedstocks could be economically feasible. It will be an effective way to utilize renewable resources to meet the growing energy demand. In-depth research along with advanced technology would be able to resolve the issues regarding capital cost and production cost in upcoming years.

Table 10
Comparative production cost of biodiesel reported from various oil feedstocks.

Feedstock oil	Biodiesel production process	Production cost of biodiesel	Country of origin	Year of estimation ^a	Reference
Pongamia oil	Base (sodium alkoxide) catalyzed transesterification	0.232 USD/L	India	2004	Barnwal and Sharma (2005)
Linseed oil	Base (sodium alkoxide) catalyzed transesterification	0.299 USD/L	India	2004	Barnwal and Sharma (2005)
Coconut oil	Base (sodium alkoxide) catalyzed transesterification	0.411 USD/L	India	2004	Barnwal and Sharma (2005)
Soya bean oil	Base (sodium alkoxide) catalyzed transesterification	0.668 USD/L	India	2004	Barnwal and Sharma (2005)
Mustard oil	Base (sodium alkoxide) catalyzed transesterification	0.852 USD/L	India	2004	Barnwal and Sharma (2005)
Sunflower oil	Base (sodium alkoxide) catalyzed transesterification	0.888 USD/L	India	2004	Barnwal and Sharma (2005)
Groundnut oil	Base (sodium alkoxide) catalyzed transesterification	1.065 USD/L	India	2004	Barnwal and Sharma (2005)
Safflower oil	Base (sodium alkoxide) catalyzed transesterification	1.109 USD/L	India	2004	Barnwal and Sharma (2005)
Sesame oil	Base (sodium alkoxide) catalyzed transesterification	1.192 USD/L	India	2004	Barnwal and Sharma (2005)
Soybean oil	Na-methoxide catalyzed transesterification	0.53 USD/L	USA	2006	Haas et al. (2006)
Rapeseed oil	Sodium methylate catalyzed transesterification	0.486 USD/L	South Africa	2008	Amigun et al. (2008)
WCO	KOH catalyzed transesterification	1.201 USD/L	Iran	2012	Mohammadshirazi et al. (2014)
JCO	KOH catalyzed transesterification	0.536 USD/L	India	2012	Nevase et al. (2012)
Palm oil	Acid (H ₂ SO ₄) catalyzed esterification and base (KOH) catalyzed transesterification	0.99 USD/L	Colombia	2013	Kirubakaran and Selvan (2018)
Sunflower oil	Base (KOH) catalyzed transesterification	0.99 USD/kg	Serbia	2013	Tasić et al. (2014)
Karanja oil	Base (KOH) catalyzed transesterification	0.999 USD/L	India	2013	Patel and Sankhavara (2017)
Pongamia oil	Base (NaOH) catalyzed transesterification	0.907 USD/L	India	2014	Doddabasawa (2014)
WCO	Acid (H ₂ SO ₄) catalyzed transesterification	750.38 USD/t	Hong Kong	2014	Karmee et al. (2015)
WCO	Base (KOH) catalyzed transesterification	868.60 USD/t	Hong Kong	2014	Karmee et al. (2015)
WCO	Lipase catalyzed transesterification	1047.97 USD/t	Hong Kong	2014	Karmee et al. (2015)
Waste chicken fat	KOH catalyzed transesterification	0.392 USD/L	India	2015	Rao and Ramakrishna (2015)
Lipid	Acid (H ₂ SO ₄) catalyzed esterification/transesterification	1232 USD/t	Spain	2016	Olkiewicz et al. (2016)
WCO	NaOH catalyzed transesterification	0.1318 USD/L	Brazil	2017	Miranda et al. (2018)
Sunflower oil	Enzymatic (lipase) transesterification	0.71 USD/L	Croatia	2017	Budzaki et al. (2018)
WCO	NaOH catalyzed transesterification	0.752 USD/kg	India	2017	Avinash and Murugesan (2017)
WCO	KOH catalyzed transesterification	0.407 USD/L	India	2018	Joshi et al. (2019)
WCO	MOF-5 catalyzed esterification/transesterification	0.738 USD/kg	México	2019	Ben-Youssef et al. (2021)
JCO	MOF-5 catalyzed esterification/transesterification	2.385 USD/kg	México	2019	Ben-Youssef et al. (2021)
Microalgae oil	Alkali (KOH) catalyzed transesterification	0.275 USD/L	Portugal	2020	Branco-Vieira et al. (2020)
<i>Calophyllum inophyllum</i> oil	Zn–CaO nanocatalyzed transesterification	0.68 USD/kg	India	2020	Naveenkumar and Baskar (2020)
Palm oil	Transesterification	0.68 USD/L	Indonesia	2020	Mizik and Gyarmati (2021)
Rapeseed oil	Transesterification	0.75 USD/L	Europe	2020	Mizik and Gyarmati (2021)
Castor oil	Zn–CaO catalyzed transesterification	0.77 USD/kg	India	2020	Naveenkumar and Baskar (2021)

^a Year of manuscript received for publication or year of analysis.

6. Life cycle assessment (LCA) of biodiesel synthesis

Though biodiesel is emerging in the global perspective as a sustainable and green alternative to fossil fuel, its conventional production processes are being questioned in terms of environmental consequences (Khounani et al., 2021; Hosseinzadeh et al., 2022). The impact on the environment by the chemicals and energy used as well as the generation of huge waste and wastewater along with other byproducts during the production of biodiesel is still challenging (Hosseinzadeh et al., 2022). However, the dry-washing process of biodiesel purification may decrease the generation of large wastewater (Ramos et al., 2019). The overall impact on the environment from the production processes starting from the extraction of feedstock from raw material, processing, manufacture, use, recycling, and disposal is of high concern in today's scientific society for considering biodiesel as a fuel for the future (Ilgin and Gupta, 2010). Life cycle assessment (LCA) is an analytical tool with a specified method used in the evaluation of the overall impact of a product, process, or human activity on the environment from material acquisition, through production and use, to waste management (Ilgin and Gupta, 2010; Curran, 2013; Brahma et al., 2022). In terms of biodiesel production, LCA can be a useful tool for evaluation of the consequences on the environment from all the input and output flow from the cultivation stage to the combustion as well as disposal of byproducts. The idea of LCA was developed in the late 1960s, but it was not widely used in different fields until the late 1980s (He and Yu, 2020). LCA analysis can reveal the environmental burden of a product at all stages in

its life cycle (Curran, 2013). LCA may play an important role in public and private environmental management concerning products. According to ISO 14040 series, the LCA consists of four stages viz. (i) Goal and scope definition, (ii) Life cycle inventory analysis, (iii) Life cycle impact assessment, and (iv) Interpretation of result (Rajaeifar et al., 2017; Khanali et al., 2020).

Regarding the environmental impact of the biodiesel production processes, several researchers examined and published literature worldwide. Because of that, from 1991 to 1994, a group of German and Dutch scientists carried out comparative studies on biodiesel to examine their impact on the environment (Spirinckx and Ceuterick, 1996). A systematic LCA on the use of biodiesel was reported by Spirinckx and Ceuterick in 1994 applying all the steps of LCA (Spirinckx and Ceuterick, 1996). Lardon et al. (2009) reported the LCA of biodiesel production from microalgae, where a comparative LCA study was undertaken to assess the energetic balance and the potential environmental impact of the whole process chain, from the biomass production to the biodiesel combustion. In the goal and scope definition, the well-to-wheel, well-to-gate, cradle-to-gate, cradle-to-grave, etc., are some of the system boundary considerations in the LCA of biodiesel (Dufour and Iribarren, 2012; Fernandez et al., 2016; Khoshnevisan et al., 2018; Liu et al., 2018c; Khounani et al., 2021). The functional unit consideration for LCA of biodiesel is reported to be 1000 kg of biodiesel, 1 MJ of biodiesel, etc. (Dufour and Iribarren, 2012; Fernandez et al., 2016; Liu et al., 2018c; Al-Muhtaseb et al., 2021). In life cycle inventory analysis of biodiesel, two types of data are reported to be required viz foreground and

background, in which material and energy used in the process is included in foreground data, and the data obtained from production and processing of materials and energy carriers are considered as background data (Aghbashlo et al., 2020; Khoshnevisan et al., 2020; Khou-nani et al., 2021). Abiotic depletion, abiotic depletion (fossil fuels), ozone layer depletion (ODP), global warming potential (GWP), freshwater aquatic ecotoxicity, human toxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, eutrophication, potential acidification, etc. are some of the environmental impact categories reported with an emphasis in LCA of biodiesel (Peiró et al., 2010; Chung et al., 2019; Aghbashlo et al., 2020; Al-Mawali et al., 2021). A comparative life cycle impact assessment of biodiesel synthesis using different catalysts is listed in Table 11. The transesterification stage in biodiesel production showed a greater impact of 68% in the system (Peiró et al., 2010). The abiotic depletion potential in all these cases is found to be insignificant, whereas a large variation in the GWP was noticed. The least GWP of 0.32 kg CO₂ eq was reported by Ripa et al. (2014) for WCO catalyzed by KOH, whereas a comparatively large GWP of 4051 was reported by Harding et al. (2008) for rapeseed oil catalyzed by NaOH. In terms of human toxicity, Al-Muhtaseb et al. (2021) reported 157.551 kg 1,4-DB eq for bifunctional CaO/CeO₂ catalyst for the conversion of waste loquat oil to biodiesel which was found to be high followed by 145 and 134 kg 1,4-DB eq for rapeseed oil catalyzed by NaOH and enzyme, respectively (Harding et al., 2008; Al-Muhtaseb et al., 2021). In most of this reported LCA of biodiesel synthesis (Table 11), the catalyst used was alkali and non-recyclable. Al-Mawali et al. (2021) reported the recyclability of magnetic Fe₂O₃ catalyst up to four times for reaction of waste date oil.

Chung et al. (2019) showed the recyclability of up to the 5th cycle for eggshell-derived CaO catalyst in biodiesel synthesis. Very good recyclability of 18 times of bifunctional CaO/CeO₂ catalyst was reported by Al-Muhtaseb et al. (2021). As already mentioned, the MOF is emerging as an efficient catalyst in biodiesel synthesis due to its excellent physical properties like high surface area, uniform porosity, and efficient catalytic and recyclability.

Regarding the LCA of the production processes of MOFs, a cradle-to-gate approach was reported by Grande et al. (2017) where four different production processes were shown. They considered climate change, freshwater eutrophication, particulate matter, and resource depletion (mineral, fossil, and renewable) as the environmental impact categories for the LCA. This study showed that the production process with the least value in these impact categories was considered suitable in terms of environmental concerns. As per the report, the production process utilized water as the solvent instead of organic solvent and was able to reduce two orders of magnitude of emission of CO₂ as well as one order of freshwater toxicity and resource depletion. In a similar study, Luo et al. (2021) reported the LCA of solvothermal and aqueous solution-based production of MOF UiO-66-NH₂ considering GWP (kg CO₂ eq), particulate matter (kg PM10 eq), terrestrial acidification (kg SO₂ eq), freshwater eutrophication (kg P eq), human toxicity (kg 1,4-DCB eq), and water scarcity (m³) as the environmental impact categories. The result of the LCA showed minimum impact from the aqueous solution-based production process and accordingly, emphasized for the same. Consequently, for consideration of the sustainability of a product in terms of environmental implication, LCA may be a profound tool with

Table 11
Comparative life cycle impact assessment of biodiesel synthesis using different catalysts.

Impact category	Unit	Feedstock materials used in biodiesel synthesis									
		Al-Mawali et al. (2021)	Aghbashlo et al. (2020)	Chung et al. (2019)	Al-Muhtaseb et al. (2021)	Peiró et al. (2010)	Ripa et al. (2014)	Ripa et al. (2014)	Harding et al. (2008)	Harding et al. (2008)	Soraya et al. (2014)
Catalyst used	–	Magnetic Fe ₂ O ₃ nanoparticle	KOH	Eggshell derived CaO	Bifunctional CaO/CeO ₂	Acid and base	KOH	KOH	NaOH	Enzyme	NaOH
Biodiesel feedstock	–	Waste date oil	Waste cooking oil	Waste cooking oil	Waste loquat oil	Used cooking oil	Waste cooking oil	Rapeseed oil	Rapeseed oil	Rapeseed oil	Palm oil
Abiotic depletion	kg Sb eq	0.00	–	6.93 × 10 ⁻²	0.00	5.51	4.66 × 10 ⁻³	1.11 × 10 ⁻²	16	15.4	1.32
Abiotic depletion (fossil fuels)	MJ	812.09	–	–	15657.48	–	–	–	–	–	–
Global warming potential	kg CO ₂ eq	48.18	–	8.23	541.323	2.99.60	0.32	2.62	4150	4050	28
Ozone layer depletion	kg CFC-11 eq	0.00	9.50 × 10 ⁻¹⁰	8.09 × 10 ⁻⁷	0.00	5.80 × 10 ⁻⁵	–	–	8.27 × 10 ⁻⁴	7.77 × 10 ⁻⁴	–
Human toxicity	kg 1,4-DB eq	20.96	–	1.10	157.551	106.97	9.66 × 10 ⁻²	1.12	145	134	–
Freshwater aquatic ecotoxicity	kg 1,4-DB eq	26.69	3.07 × 10 ⁻¹	1.62 × 10 ⁻¹	44.981	19.18	–	–	14.1	12.4	–
Marine aquatic ecotoxicity	kg 1,4-DB eq	78797.35	–	6.10 × 10 ²	174943.45	1.39 × 10 ⁵	–	–	2.77 × 10 ³	2.52 × 10 ³	–
Terrestrial ecotoxicity	kg 1,4-DB eq	0.06	3.52 × 10 ⁻²	1.00 × 10 ⁻²	0.039	0.52	–	–	2.71	1.72	–
Photochemical oxidation	kg C ₂ H ₄ eq	0.01	–	7.75 × 10 ⁻⁴	0.164	0.08	7.58 × 10 ⁻⁵	1.18 × 10 ⁻³	1.45	1.43	0.146
Acidification	kg SO ₂ eq	0.26	4.49 × 10 ⁻⁵	1.18 × 10 ⁻²	2.604	1.39	1.19 × 10 ⁻³	1.70 × 10 ⁻²	30.2	29.3	1.417
Eutrophication	kg PO ₄ ³⁻ eq	0.17	2.02 × 10 ⁻⁶	1.48 × 10 ⁻³	0.084	0.10	1.74 × 10 ⁻⁴	5.47 × 10 ⁻³	37.5	37.5	0.673

efficiency. In this regard, the production process, efficiency in catalysis as well as recyclability may influence a lot in connection to the sustainable environment-friendly product for the future. Thus, LCA of MOF catalyzed production of biodiesel and comparative analysis with other reported catalysts may bring a notion in the utilization of MOF as a sustainable catalyst for biodiesel production.

7. Latest trends in production of biodiesel

7.1. Applications of machine learning technology in biodiesel synthesis

In addition to transesterification, three other processes are applied for the production of biodiesel and these are direct use and blending, microemulsion and pyrolysis (Amin, 2019; Tabatabaei et al., 2019; Bashir et al., 2022). Machine learning (ML) technology applications in the biodiesel production processes are getting more important in recent times. ML technology is classified based on various aspects that include catalyst type, feedstock type, reactor type, operation mode, and process intensification method. Multilayer perceptron neural network (MLPNN), Support vector machines (SVM), Bayesian regularized neural network (BRNN), Adaptive network-based fuzzy inference system (ANFIS), Least square support vector machine (LSSVM), Simulated annealing (SA), Particle swarm optimization (PSO), Kernel-based extreme learning machine (KELM), Principal component analysis (PCA), Genetic algorithm (GA), Extreme learning method (ELM), Cuckoo search (CS), Artificial neural network (ANN), and linear regression (LR) are some powerful machine learning algorithms applied for predicting different parameters of biodiesel research (Aghbashlo et al., 2021; Ahmad et al., 2021; Zhong et al., 2021; Brahma et al., 2022). Different algorithms have varied prediction efficiency. According to the biodiesel research works published so far, the ML technology applications are mainly divided into five different classes which are mechanically-assisted, supercritical alcohol, enzyme-catalyzed, ultrasound-assisted, and microwave-assisted transesterification methods.

7.1.1. Mechanically-assisted transesterification process

In this process, the reaction of oils or FFAs and alcohol is carried out in a batch reactor in the presence of a suitable catalyst. The reactants are firstly heated up to the desired temperature followed by their blending using a mechanical stirring tool. Different variables that influence the biodiesel yield in mechanical stirring reactors are reaction temperature, residual time, mixing intensity, type and quantity of catalyst, ATOR and reactors. Many researchers tried to compare the capability of the MLPNN approach with the RSM in modeling the mechanically-stirred methylation process of various oils catalyzed by different acid and base catalysts (Kumar et al., 2017; Ofoefule et al., 2019; Esonye et al., 2020; Garg and Jain, 2020; Lakshmi et al., 2020). They all concluded that the designed MLPNN technique could effectively model the FAME yield compared to the RSM technique. On the other hand, some researchers found that the prediction capability of the RSM method was better than the MLPNN approach in some investigations. Kavitha and Murugavelh (2019) reported that the quadratic RSM was much more precise than the MLPNN model in predicting the FAME yield from the degummed *Sterculia foetida* oil in the presence of KOH catalyst under mechanical agitation. Etim et al. (2018) and Dharma et al. (2017) coupled the MLPNN approach with the GA paradigm and found it to be capable to optimize the transesterification of non-edible oils under mechanical agitation. Hariram et al. (2019) combined the BRNN model with the GA approach to optimize the reaction conditions of the esterified CIO. It was found that the developed MLPNN-GA and BRNN-GA techniques could successfully model and adequately estimate the ORCs. Nasef et al. (2016) combined the MLPNN approach with the SA algorithm to model the process yield and optimize the reaction conditions of triacetin transesterification under mechanical stirring. The developed MLPNN-SA approach could successfully predict and optimize the process variables. Kusumo et al. (2017) evaluated the estimation

power of the KELM approach in comparison with the MLPNN regressor in generalizing the process yield of the mechanically-assisted transesterification of the esterified *Ceiba pentandra* oil. Sohpal et al. (2011) found that the developed ANFIS model could accurately predict the biodiesel yield of JCO during the mechanically-assisted butylation process. Ighose et al. (2017) successfully combined the ANFIS approach and the GA paradigm to optimize the methylation process of the esterified yellow oleander oil under mechanical agitation. Ishola et al. (2019) coupled the RSM, MLPNN, and ANFIS approaches with the GA paradigm to model the process yield and optimize the reaction conditions of the esterified *Hibiscus sabdariffa* oil under mechanical agitation. The most promising modeling and optimization results were obtained using the ANFIS-GA combination. Betiku and Ishola (2020) compared the predictive accuracy of the MLPNN and ANFIS methods for generalizing the biodiesel yield of the esterified sorrel oil in the presence of a heterogeneous base catalyst. The ANFIS model coupled with the GA method was successful to find out the ORCs. Kumar et al. (2018) and Sajjadi et al. (2016) compared the capacity of the RSM and ANFIS techniques in estimating the biodiesel yield during the base-catalyzed process of non-edible feedstocks under mechanical agitation. The developed ANFIS models slightly outperformed the RSM models.

7.1.2. Supercritical alcohol transesterification process

Biodiesel production via the supercritical method is a promising process for the low-quality FFA-rich feedstocks. In this process, the density of alcohol is increased while its dielectric constants are decreased under supercritical conditions supporting the formation of triglycerides and alcohol as a single uniform phase. This technique has various advantages over the mechanical stirring method including no requirement of catalyst separation and no soap formation, shorter reaction time, no sensitivity towards FFAs and water present in the feedstocks. However, this process also has a few drawbacks. The process requires high pressure and temperature and high ATOR (Saka and Kusdiana, 2001). Farobie et al. (2015) confirmed the generalization capability of the MLPNN model for predicting the biodiesel contents of canola oil under supercritical ethanol/methanol conditions. Farobie and Hasanah (2016) precisely predicted the biodiesel yield of canola oil under supercritical methyl *tert*-butyl ether conditions using the MLPNN model. Furthermore, the MLPNN technique designed for modeling the FAME contents of microalgae and mahua oils outperformed the developed RSM model (Srivastava et al., 2018). Selvan et al. (2018) developed the ANN-GA model which was able to predict the optimum biodiesel content synthesized from *Aegle marmelos* oil and ORCs.

7.1.3. Enzyme-catalyzed process

Low-quality feedstocks with high amounts of FFAs and water can be efficiently converted into biodiesel in the presence of heterogeneous enzymatic catalysts. This process has lower energy consumption since the reaction can be performed under mild conditions. The enzymes mainly lipases obtained from biological systems can be used in immobilized or soluble form. However, the high enzyme cost and longer reaction time make it economically impracticable (Tabatabaei et al., 2019). Ying et al. (2008) considered the MLPNN modeling system for predicting the FAME yield during the esterification of the saponified and acid-treated rapeseed oil in the presence of *Candida rugosa* lipase. The developed MLPNN model was able to estimate the biodiesel yield with acceptable accuracy. Karimi et al. (2016) applied the MLPNN and RSM models for estimating the process yield and energy efficiency during biodiesel synthesis from WCO using lipase immobilized onto magnetic nanoparticles. The developed MLPNN model was better than the RSM model for predicting the output variables. Zarei et al. (2014) found that the developed RSM model was more accurate than the MLPNN model while generalizing the methylation process of JCO in the presence of immobilized lipase-catalyst. Amini et al. (2017) applied the MLPNN and GA combination to model and optimize the sweet basil oil methylation process catalyzed by Novozym 435. This model was effective for

predicting the process yield and ORCs. Hajar and Vahabzadeh (2014) could estimate the FAME yield of the castor oil esterification using Novozym 435 catalyst employing ANN modeling.

7.1.4. Ultrasound-assisted transesterification process

Ultrasound can be classified into high-frequency (1000–10,000 kHz) and low-frequency (20–100 kHz) sound. The introduction of ultrasonic irradiation in the transesterification process leads to cavitation of bubbles close to the alcohol-oil phase boundary (Aransiola et al., 2014). The consequent cyclic formation, growth, and asymmetric breakdown of the generated bubbles increase the temperature (above 5000 K) and pressure (above 1000 atm) of the reaction medium. The alcohol-oil phase boundary is disrupted due to the generation of micro-turbulence, leading to severe mixing between the immiscible reactants, and the main parameters influencing the performance of ultrasound-assisted transesterification systems are irradiation frequency, sound power, catalyst, alcohol, and reactor (Aghbashlo et al., 2017a, 2017b; Tan et al., 2019). Tan et al. (2019) found that the MLPNN model can be successfully used to estimate the biodiesel purity and yield during transesterification of the esterified jatropha oil under ultrasonic irradiation. Ideris et al. (2021) extracted oil from *Canarium odontophyllum* using the ultrasound-assisted technique and optimized the extraction process employing the RSM-based BBD model, and reported 95.2% yield of biodiesel. Maran and Priya (2015) determined that the MLPNN model was more accurate than the RSM model in estimating the FAME yield of the ultrasound-assisted reaction of the esterified non-edible oils. Rajkovic et al. (2013) reported that the developed MLPNN model outperformed the RSM model in prognosticating the process yield of the ultrasound-assisted reaction of edible oil. Thangarasu et al. (2020) found that the MLPNN model was more efficient than the RSM model in predicting the *Aegle marmelos* oil biodiesel yield. Naderloo et al. (2017) and Mostafaei et al. (2016) tried to estimate the energy ratio, productivity, and biodiesel yield from WCO under ultrasonication using ANFIS, LR, and RSM models. They concluded that all the parameters considered were accurately predicted using the constructed ANFIS model compared to the LR and RSM models. Aghbashlo et al. (2017a) applied the ANFIS technique in modeling and optimization of WCO biodiesel synthesis using a piezo-ultrasonic reactor. They could develop ANFIS models successfully to correlate energy consumption and conversion efficiency with MTOR, ultrasonication time, and reaction temperature. They reported 96.63% of conversion efficiency and the specific energy consumption was found to be 373.89 kJ/kg.

7.1.5. Microwave-assisted transesterification process

The microwave irradiation process is a solution for the problems associated with the conventional heating process (Milano et al., 2018). The wavelength and frequency of microwaves are respectively in the range of 0.01–1 m and 0.3–300 GHz. Polar molecules can absorb the irradiated microwave energy and then release the absorbed energy in the form of thermal energy. In addition, a microwave influences the molecular motions such as the ion migration/dipole rotations without affecting the molecular structure (Singh et al., 2014). Since the mixture of oil/FFA, alcohol, and catalyst contains both polar and ionic compounds, efficient and rapid heating can be achieved from microwave irradiation. This volumetric and selective heating method is an efficient method for intensifying and improving chemical reactions like transesterification due to the direct delivery of energy to the reactants (Motasemi and Ani, 2012). The separation process is simpler in the microwave-assisted process than the conventional heating process (Khounani et al., 2019). This process depends on the frequency and wavelength of the electromagnetic field, alcohol, feedstock characteristics, catalyst, and reactor. Ma et al. (2016) attempted to model the acidified oil esterification process under microwave irradiation using the MLPNN and RSM approaches. The MLPNN model exhibited better generalization capability in comparison to the RSM model. Selvaraj et al. (2019) used the MLPNN and RSM approaches for predicting the

biodiesel yield of the microwave-assisted transesterification of WCO. They reported that the developed MLPNN model was more precise than the constructed RSM model in generalizing the process yield. Silitonga et al. (2020) used a combination of the ELM approach and CS algorithm to model the process and optimize the reaction parameters during microwave-assisted transesterification of *Ceiba pentandra* oil. The results confirmed that the developed approach was suitable for modeling and optimizing the reaction process. Wali et al. (2013) compared the capability of the classical fuzzy logic, ANFIS, and adaptive controllers to monitor and control a pilot-scale microwave reactor applied in producing biodiesel from WCO in real-time. They reported that the ANFIS controller is found to be more robust to variation of parameters in comparison to the Fuzzy controller.

7.2. Reactors used in biodiesel synthesis process

A reactor is one of the most important components of the transesterification process to effectively produce biodiesel from the commercial point of view. Different types of reactors are employed in the synthesis of biodiesel. These are batch stirred tank reactor (BSTR), continuous stirred tank reactor (CSTR), microwave reactor, ultrasonic reactor, annular centrifugal contactor, reactive distillation reactor, shockwave power reactor, oscillatory baffled reactor, hydrodynamic cavitation reactor, spinning tube-in-tube, micro-channel reactor, fluidized bed reactor and membrane reactor (Tabatabaei et al., 2019; Brahma et al., 2022; Yaashikaa et al., 2022). Applications of various types of reactors in the production of biodiesel from different oil feedstocks along with the catalysts employed, reaction conditions, and product yields are listed in Table 12. The factors that affect the reactors based on the processing type are the temperature, residence time, heat transfer, and mass exchange. All the reactors have some merits and demerits. The batch reactor is the most commonly employed system for biodiesel synthesis at the commercial level. BSTR and CSTR are widely used for commercial-scale production due to their low-cost and simple nature though these have some disadvantages including controlling issues and low efficiency (Tabatabaei et al., 2019). Biodiesel synthesis using a microwave reactor is simple and efficient in terms of time, thermal, and control system. It has good product yields and less downstream processing but it has low reproducibility (Tabatabaei et al., 2019). The process of biodiesel production can be improved by adopting microwave or ultrasonic-assisted technologies in place of conventional stirring and heating methods, which consume less energy and induce uniform reaction conditions leading to very less process time.

8. Conclusions and future directions

The rate of any chemical reaction can be increased by employing suitable catalysts to obtain the desired products in less time. One of such prominent roles of catalysts can be seen in biorefinery industries in the production of biofuels mainly biodiesel. The transesterification and esterification reactions of oil feedstocks utilize different types of catalysts such as acidic, basic, and enzyme catalyst for facile conversion to biodiesel. Later, heterogeneous solid acid and base catalysts became ideal catalysts for both transesterification and esterification. After many years of research, scientists found MOFs as a potential heterogeneous catalyst for biodiesel production. In order to further improve the efficiency and catalytic performances, the derivatives of MOFs have been studied. Numerous hybrid materials are derived from MOFs such as micro/nanostructured catalysts, functionalized or post-functionalized hybrid catalysts, bifunctionalized catalysts, and so on. The biocompatibility and biodegradability strength of MOFs have also been considerably studied nowadays by exploring their different functionalization which can lead to their use in sophisticated biological applications.

MOFs have been synthesized as versatile composites. As reported in the literature to date, some synthesis processes of MOF composites are mainly solvothermal method and hydrothermal method. The times

Table 12
Application of various reactors in production of biodiesel from different feedstocks.

Reactors used	Biodiesel feedstock	Catalyst	Reaction conditions					Reference
			Catalyst (wt %)	Alcohol/oil	Temp (°C)	Time (min)	Yield (%)	
Ultrasonic	WCO	KOH	1	6:1	60	10	97.12	Aghbashlo et al. (2016)
Microwave	WCO	Lipase435	10	4.5:1	60	240	94	Panadare and Rathod (2016)
Hydrodynamic cavitation	WCO	KOH	1	6:1	60	15	98	Chuah et al. (2017)
Microwave	JCO	KOH	1	6:1	65	0.166	90	Lin and Chen (2017)
Ultrasonic	WCO	KOH	1	6.1:1	59.5	10	96.63	Aghbashlo et. (2017a)
Micro reactor	Sunflower oil	KOH	0.7	6:1	60	4	~99	López-Guajardo et al. (2017)
Microwave	Palm oil	[HSO ₃ -BMIM]HSO ₄ (acidic ionic liquid)	9.17	11:1	108	385.8	98.93	Ding et al. (2018)
Hydrodynamic cavitation	Yellow oleander oil	KOH	1	6:1	40–55	35	97.5	Yadav et al. (2018)
Supercritical methanol	Wet spent coffee grounds	–	–	5:1	270	20	86.33	Son et al. (2018)
Supercritical methanol	WCO	–	–	37:1	253.5	14.8	91.5	Abolazayem et al. (2018)
Packed bed	Linseed oil	CaO	160 g	9.48:1	30	27.9	98.08	Gargari and Sadrameli (2018)
Oscillatory flow	WCO	H ₂ SO ₄	1	6:1	60	30	78.8	García-Martín et al. (2018)
Oscillatory flow	Palm fatty acid Distillate	Modified sulfonated glucose	2.5	9:1	60	50	94.21	Kefas et al. (2019)
Membrane	Sunflower oil	Strontium oxide	3	12:1	65	30	>90	Hapońska et al. (2019)
Autoclave	Waste palm oil	Coconut coir husk derived solid acid catalyst	10	13:1	130	180	89.8	Thushari et al. (2019)
Packed bed	Soybean oil	Immobilized <i>Burkholderia cepacia</i> lipase	3	4:1	40	180	97.24	Murillo et al. (2019)
Packed bed	<i>Chlorella</i> sp. oil	Dodecyl benzene sulfonic acid (DBSA)	11	30:1	100	30	99	Jazie et al. (2020)
Microchannel	Refined palm oil	KOH	5	7.6:1	25	0.66	98.6	Laziz et al. (2020)
Microwave	Waste lard	CaO-zeolite	8	30:1	65	85	90.89	Lawan et al. (2020)
Fixed bed	Palm oil	Waste seashell	10	30:1	65	60	>99	Jindapon et al. (2020)
Microreactor	WCO	Calcined cow bone	8.5	2.25:1	63.1	1	99.24	Mohadesi et al. (2021)
Static mixer	WCO	Lipase	1	1:1	40	540	86.5	Gong et al. (2020)
Microwave heated continuous flow	Palm oil	Choline hydroxide (ChOH) ionic liquid	6	13.2:1	68	5	89.72	Phromphithak et al. (2020)
Continuous microwave assisted	WCO	Activated limestone-based catalyst	5.36	12.26:1	65	58.46	97.15	Ali et al. (2020)
Ultrasonic	Spent coffee ground	KOH	4	30:1	–	180	97.11	Goh et al. (2020)
Robinson-Mahoney	WCO	Calcium oxide (CaO)	8.75	8.72:1	60	120	>98.5	Soria-Figueroa et al. (2020)
Ultrasonic	WCO	Marble waste powder precalcined followed by acid treatment and calcinations	6.8	15.9:1	64.8	180	95.45	Bargoe et al. (2021)
Ultrasonic	Waste vegetable oil	CaO	1.5	6:1	70	60	98	Topare and Patil (2021)
Rotating tube	Palm oil	NaOH	1	6:1	30	180	97.5	Chanthon et al. (2021)
Batch	<i>Euglena sanguinea</i> oil (microalgae)	White mussel shell	6	0.35:1	70	80	90	Miriam et al. (2021)
Continuous stirred	Canola oil	KOH	0.5	9:1	60	60	95.13	Hasanah (2021)
Microwave	WCO	NaOH	0.8	12:1	65	2	98.4	Hsiao et al. (2021)
Microbubble	Chicken fat oil	p-Toluene sulfonic acid (PTSA)	7	13.7:1	70	30	89.90	Javed et al. (2021)
Static mixing	Palm oil	KOH	0.5	6:1	60	–	99.85	Panggabean et al. (2021)
Hydrodynamic cavitation	Safflower oil	KOH	0.94	8.36:1	–	1.06	89.11	Samani et al. (2021)
Solar	WCO	NaOH	0.75	12:1	56.5	195	82	Sivarethnamohan et al. (2022)
Hydrodynamic cavitation	Thumba oil	TiO ₂	1.2	6:1	60	60	71.8	Patil et al. (2022)
Hydrodynamic cavitation	Castor oil	KOH	1.06	9.82:1	60.3	50.86	92.27	Thakkar et al. (2022)
Ultrasonic	WCO	Chicken eggshell	6.04	8.33:1	55	39.84	98.62	Attari et al. (2022)

needed for the ultimate manufacturing of the required materials via these methods are somewhat lengthy. Later, microwave irradiation and ultrasonic technology were introduced as favorable techniques for synthesizing MOF materials owing to their efficient reaction conditions and less energy consumption. Subsequently, MOFs have been employed in various applications which include electrocatalysis, photocatalysis, purification, thermodynamics, absorption, pharmacology, gas storage,

fuel, and many more. The applications are possible on account of their large surface area, manageable pore size, alterable functionalities, chemical, and structural stability. The reason behind their excellent thermal and chemical stabilities is due to the sturdy interaction made via the self-assembly of metal ions and organic linkers. Besides, in recent years, researchers have been attracted by the capability of MOFs to perform as catalyst support in the field of solid heterogeneous catalysis.

MOFs consist of almost all the essential characteristic features required for being a novel support material to accomplish a reaction. The various reported articles summarized in this review paper distinctly propose that MOFs-supported catalysts can convert the diverse quality of oil feedstocks to biodiesel with sufficiently high yield and magnificent reusability character. The utilization of MOFs-derived catalysts with abundant raw materials would make the biodiesel conversion process cost-efficient thereby making them more environmentally friendly as compared to commercial solid heterogeneous catalysts. Although MOF composites have been proven to be versatile support materials for catalysis, there are certain noteworthy points to be explored in the days to come. It is observed that despite producing sufficient yield, the catalytic activity tends to be reduced after subsequent reuse. This indicates the insufficient diffusion of reactants onto the surface of the catalyst which needs to be resolved further. The separation issue can be further improved by synthesizing a more efficient magnetic composite by attaching certain magnetic NPs to the support. The harsh reaction conditions associated with acidic MOF catalysts like excess alcohol, and high reaction temperature make them unappealing for large-scale production. The appropriate metal clusters and organic linkers need to be investigated to provide exceptional stability and performance with the purpose of mass production in industrial arenas. The enzyme immobilized MOF derivatives have gained a lot of attention in biocatalysis owing to high stability, recyclability, and catalytic activity. Nonetheless, the utilization of certain enzymes yet remains uneconomical. A thorough comprehension of the interaction between MOFs and enzymes must be adopted to fabricate superior catalysts in biomedical sciences as well as in biodiesel synthesis. The pivotal research and methodical survey related to their properties, functionalities, interaction, and performances should be aggrandized further to make MOFs a supreme composite in catalysis and multiple other applications.

Basic MOFs and bifunctional MOFs catalysts are suitable catalysts for biodiesel synthesis at the industrial scale. MOF composites are found to be promising support for bifunctional catalysts and these could be further developed to provide superior sites for both the basic and acidic functionalized groups for simultaneous transesterification and esterification. Further, the development of magnetic MOF bifunctional composites with nano-size structures will be one of the potential areas of biodiesel research for efficient activity and easy recovery and separation process. A continuous supply chain system of raw feedstocks is the need of the hour to make biodiesel a sustainable fuel for the future and to minimize the ever-increasing demand and consumption of fossil fuels to some extent. Application mixed oil (hybrid oil) including non-edible and waste oils should be emphasized for biodiesel synthesis with MOFs catalyst systems. Subsidies must also be provided to biodiesel production plants and industries to economically compete with conventional fuels. The utilization of reactors such as microwave and ultrasound-assisted systems for the synthesis of both catalyst and biodiesel is increasingly encouraged to make the process more cost-effective. Besides, applications of machine learning techniques will further boost the entire biodiesel research in modeling and optimization of the process. Considering the distinctive qualities possessed by MOF catalysts, we can say that biodiesel production utilizing these catalysts with the help of easily available feedstocks could be economically feasible. Biodiesel has the capability of replacing fossil fuels in the near future if improvements are made to resolve the constraints associated. Comprehensive and rigorous research with help of advanced technology is still needed to tackle certain harsh reaction conditions associated with biodiesel production and to explore more diversified properties of MOFs with superior catalytic activity.

CRediT authorship contribution statement

Siri Fung Basumatary: Conceptualization, Investigation, Writing – original draft. **Khemnath Patir:** Writing – review & editing. **Bipul Das:** Writing – review & editing. **Pankaj Saikia:** Writing – review & editing.

Sujata Brahma: Writing – review & editing. **Bidangshri Basumatary:** Writing – review & editing. **Biswajit Nath:** Writing – review & editing, Formal analysis. **Bhimraj Basumatary:** Formal analysis. **Sanjay Basumatary:** Conceptualization, Investigation, Supervision, Writing – review & editing.

Declaration of competing interest

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

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Glossary

Å: Angstrom
 LCA: Life cycle assessment
 ANFIS: Adaptive network based fuzzy inference system
 LR: Linear regression
 ANL: *Aspergillus niger* lipase
 LSSVM: Least square support vector machine
 ANN: Artificial neural network
 MIL: Materials of Institut Lavoisier
 AOL: *Aspergillus oryzae*
 ML: Machine learning
 ASTM: American society for testing and material
 MLPNN: Multilayer perceptron neural network
 ATOR: Alcohol to oil ratio
 MOFs: Metal organic frameworks
 BA: Butyric acid
 MTOR: Methanol to oil ratio
 BCL: *Burkholderia cepacia* lipase
 MTOAR: Methanol to oleic acid ratio
 BDC: Benzene-1, 4-dicarboxylic acid
 NO_x: Oxides of nitrogen
 BET: Brunauer–Emmett–Teller
 NPC: Nanoporous carbon
 BJH: Barrett–Joyner–Halenda
 NPs: Nanoparticles
 BRNN: Bayesian regularized neural network
 OA: Oleic acid
 BSTR: Batch stirred tank reactor
 ORCs: Optimum reaction conditions
 BTC: Benzene-1, 3, 5-tricarboxylic acid
 PA: Palmitic acid

CALB: *Candida antarctica* lipase B
 PCA: Principal component analysis
 CCD: Central composite design
 PDMS: Polydimethylsiloxane
 CIO: *Calophyllum inophyllum* oil
 PMA: Phosphomolybdic acid
 COFs: Covalent organic frameworks
 PO: Palm oil
 CS: Cuckoo search
 POM: Polyoxometalate
 CSTR: Continuous stirrer tank reactor
 PSO: Particle swarm optimization
 CVD: Chemical vapor deposition
 PTSA: p-Toluene sulfonic acid
 Ea: Activation energy
 RCO: *Ricinus communis* oil
 ELM: Extreme learning method
 RML: *Rhizomucor miehei* lipase
 FAME: Fatty acid methyl esters
 RO: Rapeseed oil
 FFAs: Free fatty acids
 RSM: Response surface methodology
 FTIR: Fourier transform infrared spectroscopy
 RT: Room temperature
 GA: Genetic algorithm
 SA: Simulated annealing
 GTA: Glyceryl triacetate
 SEM: Scanning electron microscopy
 HPA: Heteropoly acid
 SFO: Sunflower oil
 HPMo: Phosphomolybdic acid
 SO: Soybean oil
 HPW: Phosphotungstic acid
 SVM: Support vector machines
 HSC: Heterogeneous solid catalysts
 TEM: Transmission electron microscopy
 HSC: Heterogeneous solid catalysts
 TGA: Thermogravimetric analysis
 HSiW: Silicotungstic acid
 WCO: Waste cooking oil
 JCO: *Jatropha curcas* oil
 wt: weight
 KELM: Kernel-based extreme learning machine
 XRD: X-ray diffraction
 LA: Lauric acid
 ZIF: Zeolite imidazolate framework



Biodiesel production from mixed oils: A sustainable approach towards industrial biofuel production

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ABSTRACT

Biodiesel is considered eco-friendly, biodegradable, non-toxic, and carbon-neutral fuel. It is made from edible or non-edible oil feedstocks including other triglyceride sources. The production of biodiesel depends on the availability of a particular feedstock and the cost of desired raw materials. Biodiesel is mainly produced by the transesterification process using a suitable catalyst preferably a heterogeneous catalyst as it is more beneficial in terms of reusability, recovery, product purity, and production cost as well. Various reactors are developed to produce cost-effective biodiesel at the commercial level. The latest trend in biodiesel synthesis is the application of the machine learning (ML) technique to optimize the process parameters. The application of a mixture of two or more oils as feedstock either non-edible or edible oil is emphasized for biodiesel synthesis and is presently getting more importance. In this paper, the production of biodiesel from various mixed oil (hybrid oil) is reviewed and the effects of mixed oil on the reaction, physicochemical properties, fatty acid composition, and fuel quality of the product are discussed. The study highlighted the activity of various catalysts in the reaction of mixed oil and the economic feasibility. It was found that the ratio of mixed oil is an important factor in terms of conversion and quality of biodiesel. It is also revealed that the application of the ML technique is essentially useful to optimize production efficiency. The utilization of mixed oils will overcome the issues related to the non-availability of feedstocks and reduce the overall cost with improved quality of biodiesel. This approach enhances the production possibility of biodiesel at a large-scale and may boost the biorefinery sector satisfying the future energy demand if the research at the advanced level goes in the right direction.

1. Introduction

Intense depletion of petroleum resources is occurring due to the huge production of petrodiesel as well as other petroleum-based products. The massive energy demand arises due to an upsurge in industrialization, transportation, urbanization, and rapid population growth. This is causing the exhaustion of non-renewable fossil resources, and simultaneously, human civilization is climbing towards the peril of energy crisis [1,2]. Alongside, the combustion of fossil fuels is contributing mostly towards the environmental pollution by emissions of greenhouse gases and is causing global warming [1,3]. Fuels are the major source of modern-day living, concerning from simple cooking to running heavy

machineries, and the major demand in this regard is being satisfied by fossil fuels [1,3]. Society is dependent directly on fuel for continuity as well as development. The studies predicted that there will be rapid increase in energy demand by 2030 and there will be no fossil fuels for human utilization by 2060 [4,5]. Concerning the present deteriorating situation, the scientific community is searching and developing alternate energy sources to substitute fossil fuels, along with focusing on renewability and environmentally friendliness. Researchers are strengthening the methods for utilization of renewable and green energy resources such as sun, wind, hydro, ocean, and tidal for generation of energy, but none of these are satisfying the conditions for the replacement of conventional fossil fuels. Thus, a viable renewable green fuel is

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in need to survive with the present declining situation. Biofuels such as bioethanol, biodiesel, and biogas are emerging as remarkable candidates to meet the future energy demands [1]. Since the last two decades, biodiesel has been competing itself as a potent substitute to fossil fuel due to its well-comparable properties with petrodiesel [3]. Biodiesel has some advantageous features over petrodiesel such as low viscosity, high flash point, high cetane number, good lubricity, biodegradable, non-toxic, and it releases fewer greenhouse gases. It also has lower ignition delay time and high combustion efficiency which is preferable for good engine life [6–11]. Biodiesel can be used in diesel engines directly or by blending with petrodiesel with minimal engine reform [12]. Thus, biodiesel is attracting the scientific community and various researchers are working on it to make it sustainable for application among the masses.

Biodiesel is the alcohol esters of the mixture of fatty acids commonly known as FAME (fatty acid methyl esters) prepared from vegetable oils, microalgae lipids, animal fats, and sewage sludge by several processes of which transesterification is the most convenient and widely used method [13–19]. In the process, the triglyceride molecule is allowed to react with methanol mostly using a catalyst. Homogeneous, heterogeneous, and enzyme-catalyzed transesterifications are reported for biodiesel production. Along with renewability and environmental friendliness, cost-effectiveness and sustainability are important issues in searching for alternate fuel for future use. These are dependent on the availability and cost of feedstocks. Varieties of oil feedstocks such as soybean, sunflower, palm, jatropha, pongamia, yellow oleander, castor, neem, and rubber along with animal fat, microalgae lipid, sewage sludge, and waste cooking oil (WCO) are utilized for biodiesel production [1,13,16,18,20]. According to USDA-Biofuels Annual Reports 2015, the global scenario reflects the use of soybean oil (30 %), rapeseed oil (25 %), palm oil (18 %), oils from other vegetable seed (11 %), WCO (10 %) and fat (6 %) for biodiesel production [20]. However, due to the scarcity of edible oils, there is criticism over food versus fuel in utilizing edible oils as biodiesel feedstocks [21]. Accordingly, non-edible oil sources, as well as used cooking oils and edible oil industry byproducts are emphasized as potential biodiesel feedstocks. Various non-edible oil sources such as jatropha, pongamia, mahua, yellow oleander, castor, and neem are preferably reported for biodiesel synthesis with comparable properties. Usage of waste oils, oils from microalgae and animal fats are also getting important as feedstocks. In this regard, Basumatary et al [1]. reviewed and reported the synthesis of biodiesel from a variety of single oil feedstocks from non-edible and edible oil sources with well-comparable properties. The biodiesel feedstocks such as non-edible and edible oils, microalgae lipid, and animal fat possess availability constraints in bulk quantity for commercial-scale production. Due to debate for the use of edible oil in biodiesel synthesis, it has been preferably kept away from utilization as feedstock. The non-edible second-generation oils such as jatropha, pongamia, mahua, and yellow oleander are available and possess the required qualities of renewability, biodegradability, and non-toxicity, and thus, recommended as potential feedstocks. However, these feedstocks require a large area of land for cultivation to make available and sustainable [22]. The third-generation oil from microalgae is in the initial phase of development and needs extra afford for making it sufficiently available and worldwide cultivation for use as biodiesel feedstock [21]. WCO, animal and fish fat, and waste product of oil industries are also available with limited quantity.

Concerning the conflicting challenges of economic viability of the production costs of biodiesel and demerits in the application of single oil feedstocks at large-scale, researchers suggested some ways to overcome the challenges. In this regard, mixing of oils at suitable proportion before the transesterification process is recommended as one of the worthy methods, and by doing this, the insufficiency of feedstock, as well as the low-grade fuel quality, can be resolved [17,21,23]. The locally and easily available oils can be mixed for use as potential feedstocks for industrial-scale biodiesel production. However, the application of this method in a sustainable manner depends on the resultant yield obtained

after transesterification and the quality of biodiesel produced. Therefore, the objective of this paper is to review and discuss the published works on biodiesel synthesized mainly from the mixed oils (hybrid oil feedstocks) using different processes and catalysts. Comparative analysis of the properties of blended oils, composition and properties of the resultant biodiesel, and the compatibility with standard biodiesel as well as petrodiesel are discussed. Moreover, the important features of biodiesel such as the cost of biodiesel production, economic feasibility, life cycle assessment, second generation feedstocks and the latest trends in biodiesel production are also discussed in this review. Publications related to this review from the highly rated scientific journals are studied including the most recent papers.

2. Methods of biodiesel synthesis

Since the inception of the diesel engine and the introduction of vegetable oil as fuel in a diesel engine by Dr. Rudolf Diesel, the process evolution of biofuel (biodiesel) has been recognized [24]. Considerable attempts have been made by many researchers to develop the methods of biodiesel production and are still in investigation to maximize the product yields, improve fuel properties and minimize the cost of production. Vegetable oils possess high viscosity, low stability against oxidation. There are four different approaches for conversion of any oil to biodiesel viz. dilution, micro-emulsification, pyrolysis, and transesterification to resolve the problems [25,26]. These methods have been developed in various ways to produce sustainable biodiesel concerning the fact of economic feasibility of large-scale production.

2.1. Dilution method

This method comprises blending or dilution that involves the mixing of vegetable or animal oils with petrodiesel in the range of 10 to 40 % (w/w) to use as fuel in diesel engines [22]. Literature reveals that some researchers accomplished the successful blending of vegetable oils with diesel. Nye et al [27]. reported the use of neat vegetable oil or oil blended with diesel as fuel during World War II in Europe. Cater Piller Brazil Company in 1980 successfully maintained the total power using 10 % vegetable oil blended with diesel in the pre-combustion chamber without any modification of the engine. The blending of vegetable oil with diesel in the ratio of 20:80 was reported with successful results. They also reported that a mixture of 5 % diesel with 95 % of used cooking oil was explored successfully in the diesel engine in 1982 [28]. Pramanik et al [29]. reported the use of 50 % blended *Jatropha curcas* oil (JCO) to operate the engine without any major operational difficulties. After several attempts by researchers, in August 1982, a discussion regarding the development of methodology and limitation on the use of vegetable oil as fuel was undertaken in the conference of Fargo, North Dakota [24,30]. Dilution or blending is found to be comfortable only for liquid nature-portability and heat content (approximately 80 %) of diesel fuels. Blending is not suitable for oils with higher viscosity, high unsaturated carbon chain, and low volatility. There are several associated issues with the utilization of 100 % vegetable oil in the engine such as coking and trumpet formation, carbon deposition, oil ring sticking and thickening as well as gelling of lubricating oil for compatible use of vegetable oil as fuel [28,31]. A generalized technology for overcoming these issues in an economical way of biodiesel production is the point of emphasis for exploration as an alternative fuel for the future.

2.2. Micro-emulsification

Micro-emulsification involves the solubilization of vegetable or animal oils with alcoholic solvents and surfactants. The formation of micro-emulsions using various alcoholic solvents (methanol, ethanol, butanol, and hexanol) with colloidal microstructures (1-150 nm in dimensions) is the potential requirement for solving the problem of vegetable oil viscosity [22]. Micro-emulsions are defined as transparent,

optically isotropic, clear, and stable colloidal dispersions thermodynamically and the diameter of the dispersed phase droplets or particles are in the range of 100 to 1000 Å. The dispersion may be of surfactant, water, oil, and small amphiphilic molecule called co-surfactant. Micro-emulsions have lower heating values than diesel fuels due to the high alcohol contents. But the alcohols exhibit very high latent heat of vaporization that reduced nozzle coking because they cool the combustion chamber. It was proven that the viscosity was reduced to 11.2 mm²/s at 25 °C by using 2-octanol as an amphiphile in the micellar solubilization of methanol in triolin with soybean oil [32]. However, accumulation of carbon around the tubes of injector nozzle and valves was reported on applying a fuel that was done micro-emulsification with oil, methanol, 2-octanol, and cetane improver in the ratio of 52.7:13.3:33.3:1 [33]. The micro-emulsification fuel has a low cetane number that creates incomplete combustion [31]. Accordingly, an advanced procedure for conversion to biodiesel apart from the utilization of micro-emulsification is a foremost need in the biorefinery sector.

2.3. Pyrolysis

Synthesis of biodiesel through pyrolysis involves the pre-heating of vegetable oil, animal fats, and any triglycerides or fatty acid components at high temperatures (300-1300°C) in absence of oxygen or air. This technique incorporates a change in the structure of the long-chain and saturated compounds, and cleavage of chemical bonds yielding small molecules. The thermal cracking may occur in the absence or with the aid of a catalyst. Thermal decomposition of vegetable oil produces alkanes, alkadienes, aromatics, alkenes, carboxylic acids, and small amounts of gaseous products. Depending on the temperature range of pyrolysis, it is classified into three categories viz. conventional pyrolysis (550-900 K), fast pyrolysis (850-1250 K), and flash pyrolysis (1050-1300 K) [34-36]. Pyrolysis is considered to be simple, highly effective, generates no wastes, and is eco-friendly. Biodiesel produced by pyrolysis has comparable fuel properties such as low viscosity, high cetane number, acceptable corrosion rate for copper and concentration of sulfur, and water and sediment content is within limits. However, the ash content, carbon residues, and pour points of the product are undesirable [37]. The requirement of high energy for pyrolysis and other limitations compel the scientific community to search for more suitable techniques for the cost-effective production of biodiesel.

2.4. Transesterification

According to the American society for testing and materials (ASTM), biodiesel is an alkyl ester mixture of long-chain fatty acids obtained via transesterification of triglyceride [38-43]. Transesterification is one of the most convenient methods for biodiesel production that involves the transformation of vegetable oil or any triacylglycerol with alcohol in presence of a catalyst forming alkyl esters (biodiesel) and glycerol [22, 28]. Stoichiometrically, a 3:1 alcohol to oil ratio (ATOR) is needed for reaction completion. Transesterification is a reversible reaction and the alcohol in excess amount is required to shift the equilibrium to the product side. Commonly reported alcohols for transesterification in biodiesel synthesis are methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol is widely and preferably used because of its low cost, polarity, and having the shortest chain. A range of catalysts used in biodiesel synthesis is homogeneous acids and bases, enzymes, and heterogeneous solid acids and bases [26]. Base catalyzed transesterification is about 4000 times faster than acid-catalyzed transesterification. ATOR, reaction temperature, type of catalyst used and its load (%) are the main factors that influence the reaction [3,35]. Several researchers have investigated the processes of biodiesel synthesis and reported that the most preferable one is transesterification [44]. Biodiesel produced via this method has the fuel property within the limits of EN 14214 and ASTM D6751 standards. This process showed fuel properties with higher cetane numbers, lower emissions, and higher combustion efficiency.

However, the requirement of excess methanol is the major demerit of transesterification [31]. The search for suitable conditions for transesterification as well as efficient cost-effective and environmentally friendly catalysts is a prime issue for industrial-scale production of biodiesel.

3. Different types of reactors

The probable peril of energy crisis especially fuel due to the diminishing of fossil fuel brings a situation to think for an alternative fuel like biodiesel. Biodiesel is renewable and environmentally benign and is gaining a lot of attention. It is produced by various methods using vegetable oil and animal fat as the primary feedstock with the help of a suitable catalyst. To overcome the number of demerits associated with commercial production of biodiesel such as the requirement of a large amount of methanol to oil ratio (MTOR) and time consumption, reactors are developed. Reactors are tanks that consist of heating counterparts and a motor. They reduce time consumption, make the process partially or fully automated and enhance the mass transfer for biodiesel production on a commercial scale. Biodiesel reactors are classified into two classes, viz. Batch reactors and Continuous flow reactors [45]. Initially, Batch reactors were widely administered for the large-scale synthesis of biodiesel [46]. In Batch reactors, the reactants are fed into the tank at fixed reaction conditions [47]. The synthesis was cheap, but showed disadvantages such as a change in chemical composition with time, small tank size and excess separation process requirement [46]. In order to overcome the disadvantages, continuous flow reactors are designed to have good mixing efficiency of reagents and efficiency in process parameters [45]. In continuous reactors, smaller amounts of reactants are required to be added into the vessel after which the vessel continues to add ingredients [45]. Such reactors owe to biodiesel production for a commercial scale with good quality, and low capital and operating cost. Comprehensive analyses of the advantages and disadvantages of the use of reactors in biodiesel synthesis are listed in Table 1.

3.1. Batch reactor

Batch reactors are the most flexible and cheap for biodiesel production. They contain tanks or vessels that are equipped with different kinds of agitation. The reactant is filled in tanks and operated with agitation for certain duration. After certain duration, the contents of the tank are removed from which fatty acid esters and glycerol are separated resulting in two products that are further processed as biodiesel as well as value-added products [45,54].

3.2. Continuous flow reactor

A continuous stirred-tank reactor (CSTR) built with the continuous-flow system is the most commonly used common flow reactor. This reactor allows continuous addition of reactant and continuous withdrawal of the products. CSTR is similar to the batch reactor. However, continuous agitation is required to ensure constant temperature and chemical composition until the reaction is completed which corresponds to process control and continuous monitoring of the product quality. CSTR is capable of using more than a reactor and modifications are done to use two reactors in order to reduce the high energy consumption which results from thorough mixing of reactants [45,54].

3.3. Static reactor

Static mixers are simply designed devices that consist of no moving parts. This consists of spiral-shaped elements that are enclosed within a tube or column and promote the mixing of two immiscible liquids [48].

Table 1
Advantages and disadvantages of different reactors

Reactors	Advantage	Disadvantage	References
Batch reactor	<ul style="list-style-type: none"> • Cheap • Allows variation in feedstock type 	Small tank size Low production Intense energy required Limited mass transfer	[45,46]
Continuous flow reactor	<ul style="list-style-type: none"> • High-capacity biodiesel production • Low capital and operating cost. 	Process and monitoring required	[46,47]
Static reactor	<ul style="list-style-type: none"> • Easy to use has it has no moving parts, • Effective mixing of immiscible liquids. 	Slow reaction.	[48,49]
Micro-channel reactors	<ul style="list-style-type: none"> • Short reaction time, effective heat and mass transfer rate and high utility of surface area/volume ratio and short diffusion distance. 	Scale-up to achieve industrial production.	[50]
Oscillatory flow reactor	<ul style="list-style-type: none"> • Helpful for long duration reaction, • Increased heat and mass transfer • Short reaction time. • Ideal for solid catalyst or polymer assisted catalyst. 	Complex design and operation	[50,51,52]
Fixed bed reactor	<ul style="list-style-type: none"> • Simple reactors, • Low operating and maintenance cost. • Amount of solid catalyst determines the rate of reaction 	Purification process required High alcohol to oil molar ratio required Catalyst efficiency decreases Complex to operate	[53]
Reactive distillation column	<ul style="list-style-type: none"> • Low cost and low energy consumed • Reduced excess alcohol usage • Removal of product and formation occur simultaneously • High conversion and selectivity 	Complex to operate	[50,54]
Microwave reactor	<ul style="list-style-type: none"> • Rapid energy transfer • Fast reaction with clean products • Low energy and time consuming • Environmentally friendly 	Low reproducibility due to difficulty to control heat-force	[50,51]
Supercritical reactor	<ul style="list-style-type: none"> • Soap formation is eliminated • Rapid reaction attributing to pure and large quantity production with small reactor and limited space 	Requires high temperature and pressure.	[47]
Ultrasonic reactor	<ul style="list-style-type: none"> • Simple set-up • Low residence time • Low alcohol to oil molar ratio • Simple separation process • Energy is saved as no heat is involved. 	High reaction temperature Controlled reaction condition required	[55]
Plug flow reactor	<ul style="list-style-type: none"> • Small space and low capital required • Easy to clean 	Temperature and pressure drop Unsuitable for slow mixing reactions	[51,56]
Membrane reactor	<ul style="list-style-type: none"> • Pure and good product separation 	Slow reaction rate. Maintenance of	[53]

Table 1 (continued)

Reactors	Advantage	Disadvantage	References
	<ul style="list-style-type: none"> • Continuous product recovery • Low wastewater generation 	equilibrium liquid phase is crucial.	
Annular centrifugal contractor	<ul style="list-style-type: none"> • Easy and fast cleaning system 	Very low residence time resulting to incomplete conversion Additional processing required	[51,53]
Spinning tube-in-tube reactor	<ul style="list-style-type: none"> • Fast reaction rate • Low residence time • Small and easy to scale-up 	Difficulty in heating and loading of catalyst Low conversion Inappropriate mixing	[48,57]
Hydrodynamic cavitation reactor	<ul style="list-style-type: none"> • Simple and low maintenance reactor • Cheap and easy to scale-up • Suitable for reaction that required rigorous reaction conditions. 	Rate of reaction is low for viscous mixture Poor downstream pressure recovery	[58,59]
Shockwave power reactor	<ul style="list-style-type: none"> • Simple and cheap • Suitable for reaction that required rigorous reaction conditions 	Poor mass transfer Loss of energy due to friction	[51,60,61]

3.4. Microchannel reactor

Microchannel reactors are of a very narrow channel where the two phases are mixed in a micro-mixer and tiny droplets are formed followed by phase separation. These reactors are very advantageous due to reduction of reaction time, fast phase separation, well blending, providing effective heat and mass transfer rate, high utility of surface area/volume ratio, and short diffusion distance [50,51].

3.5. Oscillatory flow reactor

Oscillatory flow reactors are tabular reactor that consists of orifice plate baffles spaced equally dividing the tabular reactor into single chambers and a piston that causes oscillatory flow. The oscillatory flow in the introduction of a bulk fluid in every single chamber acts like a single stirred tank reactor and causes radial and axial mixing [48,50].

3.6. Fixed bed reactor

A fixed bed reactor consists of a cylindrical column filled with catalyst pellets that allow oils and alcohol to flow through the column and transform into biodiesel. Heterogeneous catalysts are used and no separation methods for catalyst and product are required [50].

3.7. Reactive distillation column

Reactive distillations are an alternative to reactor-separation coupled technology. Reactive distillations are made of a single chemical unit within which the chemical reaction and separations of products occur concurrently. In this reactor, the top of the column is filled with vegetable oil and through the bottom, alcohol is fed as vapor. The product formed gets pumped through the bottom whereas the water by-product is distilled through the top [50].

3.8. Microwave reactor

The transesterification method is a traditional method for the synthesis of biodiesel and this process can be accelerated by a microwave

reactor. The microwave reactor uses microwave irradiation and transfers energy directly to the reactants. The source is coupled with the power supply which is enclosed within a metallic cavity applicator. The microwave irradiation is transferred to the reactor either by coaxial cables (for low power) or waveguide (for high power). Polytetrafluoroethylene, polyether ether ketone, and quartz silicon carbide are transparent or microwave adsorptive which is used for constructing reactor vessels. The reactor vessel is coupled with mechanical stirrers to produce a uniform electric field. Microwave irradiation results in polarization or reorientation of the dipole to produce thermal energy. Microwave irradiates the polar molecules that displace the electron surrounding the atom. Rotation among the molecules creates friction and thermal energy is released. Thus, this reactor produces a high and clean product under mild reaction conditions [51,57].

3.9. Supercritical reactor

Biodiesel is traditionally produced by catalytic transesterification of oils or fats. However, biodiesel can be produced by a non-catalytic transesterification reaction called the supercritical process. In the supercritical reactor, an autoclave (high-pressure reactor) is used to carry out the supercritical transesterification process. The autoclave is filled with a given amount of reactants and methanol. Heat is adjusted and supplied to the autoclave. The temperature can be measured and controlled accordingly. After completion of the reaction, the gas is vented and the product is collected into a vessel from the autoclave. In the supercritical process, the problems associated with MTOR mixture two-phase systems are eliminated and form a single phase. This process requires high pressure and temperature but the product is formed in less time with low energy requirement [55].

3.10. Ultrasonic reactor

The ultrasonic reactor uses ultrasonic waves that result in intense mixing thereby increasing the reaction rate. The energy is transferred to the fluid by ultrasonic waves which create intense vibrations due to which cavitation bubbles result. The bubbles burst to cause fluid contraction, discharging high energy that causes the ingredients to mix inside the bubble area for which the reactivity of reactants increases in less reaction time without any elevation in temperature [56].

3.11. Plug-flow reactor

Plug-flow reactors (PFR) consist of tubes or pipes through which the reagents or reactants enter through one inlet pipe and are mixed well for a specific time and flow rate before escaping through the outlet. The efficiency of mixing is increased with the help of high turbulent flow when the reactants are within the reactor pipe. The residence time and the size of the reactor can be reduced in order to adjust the flow pressure of the reactants. The laminar flow of the fluid results in the case of fluids with higher viscosity. To substitute this shortcoming, PFR is applied along with additive injective devices, mechanical or static mixers. These reactors are also known as pipe flow reactors [51,57].

3.12. Membrane reactor

A membrane reactor is a membrane-based reactor system in which membrane and chemical reactions are combined where reaction and separation take place simultaneously. Membrane reactors increase the conversion of equilibrium limited reactions by removing some products from the reactants stream via membranes [57,62].

3.13. Annular centrifugal contactors

Annular centrifugal contactor (ACC) is a reactor-based separation technique that carries out chemical reactions and centrifugal separation.

It consists of mixing inlet and separation outlet. The reactants are fed into the inlet, mixed and chemical reaction takes place in the narrow spaces between the stationary cylinder and spinning rotor. The rotor rotates in a stationary cylinder which causes high shear stress and high centrifugal separation that increases mass transfer and fast phase separation respectively [48,51].

3.14. Spinning tube-in-tube reactor

A spinning tube-in-tube reactor is also known as a rotating or spinning reactor. This type of reactor consists of a tube fixed within another hollow tube where the inner tube rotates over the outer tube. The reactants are filled in the gap between the two tubes. A sheared thin liquid film is formed when the two immiscible liquids are mixed due to Couette flow that corresponds to mass and heat transfer, and the surface area to volume is enhanced [48,51].

3.15. Hydrodynamic cavitation reactor

Cavitation is the phenomenon of formation, development, and collapse of cavities that occur in extremely small intervals of time releasing huge magnitudes of energy. Hydrodynamic cavitation reactor is one type of cavitation reactor that consists of pump and constriction orifice situated at the pump discharge. When the high fluid passes through the constriction orifice in the system, the kinetic energy or velocity increases generating pressure variation. If the pressure variation is lower than the threshold pressure, this leads to the generation of cavities which collapses when the pressure is recovered. During its passages, the fluid develops boundary layer separation and the pressure drops which responds to loss in energy. The downstream of constriction contain high-intensity fluid turbulence which depends on the magnitude of pressure drop that correlates to constriction geometry and liquids flow condition [59,63].

3.16. Shockwave power reactor

This is the type of hydrodynamic reactor that consists of rotor and stator adjusted as two cylinders are aligned at the center. The rotor consists of some cavities and rotates inside the stator. The space between the rotor and stator is called the cavitation zone where the reaction mixture (catalyst, methanol and oil) is fed, and leads to the formation of micro-cavities. The fluid pressure converts to fluid vapor pressure due to the cavities and spinning action of the rotor that leads to rapid microscopic bubble formation which then collapses due to intense rotation of the rotor resulting in shockwave. This shockwave corresponds to rapid stirring and energy release [51,61]. In the process, low-grade oil can be utilized and handled either in continuous or batch mode.

3.17. Commonly used reactors in biodiesel synthesis

The most commonly used reactors in biodiesel synthesis were continuous stirrer tank reactor (CSTR), batch stirred tank reactor (BSTR), annular centrifugal contactor (ACC), ultrasonic reactor, hydrodynamic cavitation reactor, shockwave power reactor, spinning tube-in-tube (STT), and membrane reactor [48,51,64]. The parameters that enhance the use of these reactors are the conversion, reaction temperature, mixing rate, and residence time as well as scale-up improvements. These types of reactors undergo turbulence development that enhances the mixing rate and thereby the reaction rate [51]. Nouredin et al [65]. investigated the transesterification of refined and bleach soybean oil based on a batch continuous process. They reported that high alcohol and catalyst concentrations were required, however more than 98 % conversion of oil was achieved. Darnoko et al [66]. investigated the potential of a CSTR for biodiesel synthesis from palm oil using KOH as the catalyst. They reported that the reactor could produce 97.3 % of FAME in 60 min. Hanh et al [67]. investigated the

methanolysis of triolein by ultrasonic irradiation (40 kHz). They recorded high FAME yield in 30 min of irradiation time. They established that the ultrasonic irradiation method is a promising method for the production of biodiesel due to its high mixing speed and mass transfer. Chuah et al [68]. studied biodiesel synthesis from WCO via the hydrodynamic cavitation method. They mentioned that this method is viable for biodiesel synthesis and does not require any engine alterations. Ji et al [69]. compared biodiesel synthesis from soybean oil using ultrasonic and hydrodynamic cavitation methods. They recorded that both the methods were effective and produced high yield in low residence time with energy-saving. In another study, Dubé et al [70]. reported biodiesel production from canola oil using two-phase membrane reactors for acid and base-catalyzed transesterification reactions. They recorded that the reactor was capable of separating unreacted oil from product resulting in high purity of biodiesel. Oh et al [71]. listed some of the reactors such as refractive distillation, membrane reactor, hydrodynamic cavitation reactor, and ultrasonic reactor that are cost-effective and environmentally benign. These reactors are capable of producing high yield in less residence time with no requirement of excess methanol. These reactors are also capable of quick phase separation. Furthermore, these can undergo methanol recovery which indicated that no excess equipment is required for methanol recovery [72]. Researchers have reported numbers of reactors used in biodiesel production from different feedstocks and are listed in Table 2. All the reactors have advantages and disadvantages. In the current scenario, a batch stirrer tank reactor (BSTR) is utilized for industrial-scale production of biodiesel as it is simple and cost-effective but requires the feedstock to be fed into the tank manually. However, a continuous stirrer tank reactor (CSTR) is commonly employed as it produces good quality biodiesel, requires low space and low capital with a fast reaction rate [51]. Industrial biodiesel production requires physical and chemical energy as it undergoes a series of procedure. Initially, the seeds are required to be cleaned and then extraction of oil is carried out. Storing of seeds has to be done in such a way that they do not undergo decay or mold formation. After extraction of the oil, the oil is required to be purified to remove any water contents or impurities. All such procedures require a high amount of capital and the production of biodiesel at an industrial scale can add more capital requirements. Thus, the development of suitable reactors using advanced technology for biodiesel production may bring more cost-effectiveness in the biorefinery sector.

4. Single oil feedstocks in biodiesel production and its challenges

The scientific community has studied the application of various single oil feedstocks such as edible vegetable oils, non-edible vegetable oils, animal fats, WCO, and algal oil for the synthesis of biodiesel [38, 114]. Literature reveals that more than 95 % of the global biodiesel production is reported from single edible oils such as rapeseed (84 %), palm (1 %), sunflower (13 %), soybean, and other (2 %) [37]. However, the usage of edible oil feedstocks for the production of biodiesel raises problems concerning the food versus fuel crisis. To mitigate the demand for edible oil as biodiesel feedstock, there is a need for more farmland for cultivation and this may result in the environmental destruction of vital soil resources by deforestation in the creation of cultivation land. Moreover, worldwide population growth increases the food demand leading to the increasing price of edible oils. This may affect the economic viability of the biodiesel industry with edible oil feedstock and increase the market price of food [37]. Biodiesel production from single edible oil feedstock is not feasible in the long term because of the cultivation gap and non-availability of particular types of edible oil plants for its adaptability to grow in different regions with different environmental conditions [115]. Accordingly, non-edible oil feedstocks are economically viable for biodiesel production. Some of the non-edible oils that are mostly utilized for the production of biodiesel are JCO, *Pongamia pinnata*, *Croton megalocarpus*, *Moringa oleifera*, *Aleurites*

moluccana, *Pachira glabra*, *Ricinus communis*, *Calophyllum inophyllum*, *Sterculia feotida*, *Madhuca indica*, *Sapium sebiferum*, *Aleurites fordii*, *Azadirachta indica*, *Hevea brasiliensis*, *Nicotiana tabacum*, *Crambe abyssinica*, *Thevetia peruviana*, *Sapindus mukorossi*, and *Cerbera odollam* [1,7,10,18, 22,116]. Consideration of a particular single non-edible oil as feedstock also needs an extra-large area for cultivation which would create conflict in the production of food vs fuel, and this would increase the production cost of biodiesel. The oil may also possess the characteristics like high viscosity, low volatility, higher acidity, and low yield [116]. Biodiesel from such single oil feedstock was also reported to have poor oxidation stability and poor cold flow properties. Most of the biodiesels from single vegetable oils contain flash points above 200 °C which is also higher compared to diesel fuel, but possess lower heating value due to the presence of chemically bound oxygen in the feedstock leading to lowering of heating value by 10 % [33]. A higher concentration of saturated fatty acids present in animal fats such as beef tallow, chicken fat, fish oil, pork lard, and poultry fat resulted in higher viscosity due to which the performances are poor at low temperatures [26]. Studies on biodiesel production from WCO reported the requirement of extra time and cost for purification as well as a groundwork on the collection of feedstock from different places [18,117,118]. The high yield of biodiesel from single algal feedstocks such as microalgae, miscanthus, and *Calophyllum inophyllum* may be obtained. However, the critical drawbacks associated are algal production issues and oil extraction challenges that need huge investment, sunlight, and more expenses for large-scale production [119]. Biodiesel production from single oil feedstocks faces challenges during the process of esterification and transesterification. García-Moreno et al [120]. studied biodiesel synthesis from crude fish oil containing high free fatty acids (FFAs) and reported low oxidative stability due to higher viscosity, low biodiesel yield, and difficulty due to soap formation by saponification during transesterification. Fadhil et al [121]. reported castor seed oil with high kinematic viscosity of 226 mm² s⁻¹ at 40 °C. Jurac et al [122]. mentioned the use of frying oil that contains impurities of water and reported the loss of its significant chemical contents which leads to a negative impact on biodiesel synthesis. Feedstock with a higher degree of saturation with FFA lowers fluidity at cold temperature and leads to solidification. Kumar and Sharma [114] studied the percentage of fatty acids, pour point and cloud point of different oils. They reported that *Orbignya oleifera* oil exhibited a saturated fatty acid of 84 %, cloud point of 39.04 °C and pour point of 35.58 °C, and the coconut oil showed a saturated fatty acid of 78.5 %, cloud point of 43.01 °C and pour point of 39.89 °C. The higher saturated methyl esters present in such single oil feedstock have problems in cold flow properties that affect the quality of biodiesel. The single oil feedstocks like rapeseed (*Brassica napus*), sunflower (*Helianthus annuus*), and soybean (*Glycine max* L.) showed unsaturated fatty acids of 95.19, 90.66, and 83.05 % respectively. Such feedstocks have lower oxidation stability due to the reaction of unsaturated fatty acids with atmospheric oxygen that forms hydroperoxide, sediment, and gum, and then affect the engine performance [114]. It has been reported that the produced biodiesel from single oil feedstock has poor oxidation stability (OS) and cold flow properties (CFP). The OS recorded for sunflower (1.2 h), JCO (3.2 h), castor (3.2 h), peanut (2.0 h), corn (1.2 h), pongamia (1.7 h), and bovine tallow (1.2 h) were found to be low in comparison to standard petrodiesel [21]. A fuel with poor quality in OS and CFP can cause incomplete combustion, difficulty to start in the colder region, and blocking of filters. The improvement of OS and CFP quality in fuel can be done by using additives or synthetic antioxidants, but this would consume extra and more cost. Biodiesel from individual oils has strong acid value, high iodine values, high densities, and high kinematic viscosities. These can affect carbon deposition in diesel engines, fuel-injection systems, and tank corrosion, and the polymerization also occurs during storage and combustion that results in gum formation [21, 61]. Thus, for cost-effective refinery scale production of biodiesel, selection of suitable oil feedstocks and the modification is the prime issue, and it is empathetically needed for sustainable adoption as an

Table 2
Different types of reactors used in biodiesel synthesis

Reactors used	Biodiesel feedstock	Catalyst	Reaction conditions				Highlights	References
			Catalyst (wt %)	Alcohol/oil	Temp (°C)	Time (min)		
Microwave heated continuous flow	Palm oil	Choline hydroxide (ChOH) ionic liquid	6	13.2:1	68	5	89.72	Methyl ester content increased on increasing the microwave power. [73]
Fixed bed	Palm oil	Waste seashell	10	30:1	65	60	>99	Fixed bed reactor operates with the absence of stirring. [74]
Oscillatory flow	Palm fatty acid distillate	Modified sulfonated glucose	2.5	9:1	60	50	94.21	97.1% of biodiesel conversion was achieved at oscillation frequency of 6 Hz. [75]
Oscillatory flow	WCO	H ₂ SO ₄	1	6:1	60	30	78.8	Oscillatory flow reactor produced comparatively higher conversion in half the time than stirred tank reactor. [76]
Packed bed	Soybean oil	Immobilized <i>Burkholderia cepacia</i> lipase	3	4:1	40	180	97.24	Designed a continuous-flow bioreactor consisting two elements viz. pretreatment and packed bed that ensured higher biodiesel yield. [77]
Packed bed	<i>Chlorella</i> sp. oil	Dodecyl benzene sulfonic acid	11	30:1	100	30	99	Laminar flow dominated the viscous flow. [78]
Packed bed	WCO	NCC/CaO/PVA	0.5	6:1	65	-	98.40	Mechanical damage of the catalyst was reduced by this reactor. [79]
Membrane	Sunflower oil	Strontium oxide	3	12:1	65	30	>90	Membrane of specific pore size could increase the conversion. [80]
Static mixer	WCO	Lipase	1	1:1	40	540	86.5	Fast reaction with improved biodiesel production than stirred reactor. [81]
Continuous microwave assisted	WCO	Activated limestone-based catalyst	5.36	12.26:1	65	58.46	97.15	When microwave is used, the reactants are directly heated and produces higher yield than the conventional heating reactor. [82]
Autoclave	Waste palm oil	Coconut coir husk derived solid acid catalyst	10	13:1	130	180	89.8	High biodiesel was observed at high temperature as autoclave is a closed system and can maintain high reaction temperature at high pressure. [83]
Robinson-Mahoney	WCO	Calcium oxide (CaO)	8.75	8.72:1	60	120	>98.5	Reactor was equipped with fixed catalytic basket, thermowell, ceramic fiber mantle, and three-pitched blade turbine. [84]
Ultrasonic	WCO	Marble waste powder precalcined followed by acid treatment and calcinations	6.8	15.9:1	64.8	180	95.45	Ultrasonication reduced the energy required for biodiesel production by 1.5 folds in comparison to conventional method. [85]
Ultrasonic	Waste vegetable oils	CaO	1.5	6:1	70	60	98	Ultrasonic irradiation reduces residence time due to simultaneous micro-bubbles formation and collapses. [86]
Rotating tube	Palm oil	NaOH	1	6:1	30	180	97.5	Biodiesel yield in the rotating tube reactor was promoted by modulated wavy vortex flow. [87]
Continuous stirred	Canola oil	KOH	0.5	9:1	60	60	95.13	Condensation system was applied to study system's reflux condensation effect. [88]
Microwave	WCO	NaOH	0.8	12:1	65	2	98.4	65°C was best temperature for microwave radiation to enhance reaction with shortest reaction time. [89]
Microwave	Waste lard	CaO-zeolite	8	30:1	65	85	90.89	Effective production due to synergetic effect between reactor and catalyst. [90]
Microbubble	Chicken fat oil	p-Toluene sulfonic acid	7	13.7:1	70	30	89.90	Microbubble assisted thin film enhanced the process feasibility. Further, feeding methanol with the help of microbubble enhanced the mass transfer thereby enhanced the reaction rate. [91]
Microchannel	Refined palm oil	KOH	5	7.6:1	25	0.66	98.6	High conversion in very short residence time. Passive mixing of microchannel enhanced the biodiesel production. [92]
Batch	<i>Euglena sanguinea</i> oil	White mussel shell	6	0.35:1	70	80	90	Designed 4 in 1 reactor where oil extraction and conversion under optimized reaction conditions took place. [93]
Microreactor	WCO	Calcined cow bone	8.5	2.25:1	63.1	1	99.24	Microreactor enhanced the low speed heterogeneous reaction and reduced the reaction time to 60 s. [94]
Static mixing	Palm oil	KOH	0.5	6:1	60	-	99.85	9 reactors were equipped in order to study the reactor's effect on biodiesel production. [95]
Hydrodynamic cavitation	Thumba oil	TiO ₂	1.2	6:1	60	60	71.8	The cavitation yield for this reactor was almost 27% higher than conventional method. [96]

(continued on next page)

Table 2 (continued)

Reactors used	Biodiesel feedstock	Catalyst	Reaction conditions					Highlights	References
			Catalyst (wt %)	Alcohol/oil	Temp (°C)	Time (min)	Yield (%)		
Hydrodynamic cavitation	Safflower oil	KOH	0.94	8.36:1	-	1.06	89.11	Extended rotor-stator distance decreased the shear force and blending of mixture which reduced the yield.	[97]
Solar	WCO	NaOH	0.75	12:1	56.5	195	82	Customized copper tubes and black surface reactor to trap solar energy.	[98]
Hydrodynamic cavitation	Thumba oil	TiO ₂	1.2	6:1	60	60	71.8	This method was found to be rapid and high cavitation yield (9.1×10^{-6} mol. L/J) was observed at 5 bar.	[99]
Hydrodynamic cavitation	Castor oil	KOH	1.06	9.82:1	60.3	50.86	92.27	At optimum condition, exergetic sustainability index was found to be higher than conventional and ultrasound techniques.	[100]
Hydrodynamic cavitation	Yellow oleander oil	KOH	1	6:1	40-55	35	97.5	This technique is efficient and low time consuming.	[101]
Ultrasonic	WCO	Chicken eggshell	6.04	8.33:1	55	39.84	98.62	High power increased formation and ruptures of micro-bubbles and thus increased mass transfer.	[102]
Supercritical methanol	Wet spent coffee grounds	-	-	5:1	270	20	86.33	In supercritical methanol technique, the need of biomass drying and catalyst requirement was eliminated.	[103]
Supercritical methanol	WCO	-	-	37:1	253.5	14.8	91.5	The biodiesel was heated for 30 min where the unreacted methanol was recovered via distillation. Supercritical methanol technique facilitated transesterification without involvement of catalyst.	[104]
Packed bed	Linseed oil	CaO	160 g	9.48:1	30	27.9	98.08	Co-solvent (Diethyl ether) maintained optimum conditions for continuous transesterification reaction in a packed bed reactor.	[105]
Microwave	WCO	Lipase435	10	4.5:1	60	240	94	Microwave technique reduced the methanol evaporation in addition to uniform heat transfer and increment in mass transfer.	[106]
Micro reactor	Sunflower oil	KOH	0.7	6:1	60	4	~99	Micro-reactor was 15 times faster than batch reactor. Slug flow pattern that occurred within the reactor enhanced mass transfer.	[107]
Microwave	Jatropha oil	KOH	1	6:1	65	0.166	90	Designed large scale continuous microwave reactor having microwave penetration length of 27 cm and 18 L/min of flow rate with 19,000 L/day of biodiesel output.	[108]
Ultrasonic	Spent coffee ground	KOH	4	30:1	-	180	97.11	Oil extraction and biodiesel production via ultrasonic method. Oil was extracted in 30 mins with reduced amount of solvent in comparison to conventional method.	[109]
Microwave	Palm oil	[HSO ₃ -BMIM]HSO ₄ (Ionic liquid)	9.17	11:1	108	385.8	98.93	Microwave irradiation had the capacity to reduce the reaction time and energy saving.	[110]
Hydrodynamic cavitation	WCO	KOH	1	6:1	60	15	98	Lower feedstock and lower energy consumed (about 4.6 fold and 6 folds, respectively) by hydrodynamic cavitation in comparison to mechanical stirring.	[111]
Ultrasonic	WCO	KOH	1	6:1	60	10	97.12	High frequency ultrasonic system is replaced by piezo-electric based ultrasonic reactor.	[112]
Ultrasonic	WCO	KOH	1	6.1:1	59.5	10	96.63	Piezo-electric based ultrasound technique appeared as energy efficient and time-saving reactor for large scale production.	[113]

alternative fuel for the future.

5. Mixed oil feedstocks for biodiesel production and the advantages

To overcome the constraints of single oil feedstock-based biodiesel production, researchers suggested some approaches of which mixing of two or more vegetable oils as biodiesel feedstocks. This may resolve the problems by improving the quality of produced biodiesel, lowering raw material costs as well as the availability issues that eventually reduce the

production cost. The mixing of oil feedstocks can meet the challenges faced by single oil feedstocks and has the potential for large-scale production of biodiesel. Mixing of oil feedstocks such as castor oil, karanja oil, and JCO along with cheaper low-quality oil like WCO reduces feedstock cost, and mixing of those in proper ratio can improve the fuel quality. The synthesized biodiesel from the mixture of oil feedstocks can develop the OS and CFP without adding any additives. The concept of mixing oils having high viscosity with low viscosity makes the feedstock mixture suitable to synthesize biodiesel with good fuel properties comparable to ASTM standard [21,123]. Different oils mixed in appropriate

proportions having oils with low viscosity and moderate density, and adjusting low acid value oil with high acid value make it more suitable for quality biodiesel production. Such mixing reduces the additional cost of the esterification process as well as the time required before the transesterification [124–126]. Mixing of oil feedstocks in the optimum ratio is a significant approach, for example, 3:7 of canola oil (higher % of unsaturated fatty acids) and lard (higher % of saturated fatty acids), and this makes a more suitable chemical composition of the feedstock mixture to get better quality of biodiesel properties [127,128]. Thus, research and development in the mixing of oil feedstocks in a suitable ratio will bring hope in biorefinery exploration in terms of availability of feedstocks, reduction of production cost, and improvement in the quality of produced biodiesel.

6. Physicochemical properties of mixed oils

A variety of oil feedstocks such as non-edible and edible oils, algae oil and animal fats are reported for biodiesel synthesis. The selection of raw material is emphasized based on the availability and suitability for engine performance. The accountability of biodiesel properties is based on the physicochemical properties of the oil feedstocks. All the properties of biodiesel are the predetermined factors of assurance in using as the fuel in diesel engines [22,23,38]. A comprehensive summary of physicochemical properties of mixed oil feedstocks along with the single oil component properties is presented in Table 3. It is observed that mixing two or more single oils can improve the quality of the various physicochemical properties which in turn can improve the fuel quality of produced biodiesel [121,126,133]. To ensure efficient engine performance, the fuel must meet the biofuel standards. The United States (ASTM 6751-3) and European Union (EN 14214) standards are the most worldwide accepted standards for biodiesel. The quality of biodiesel and its properties are dependent on the FFA content of the raw oil or oil blend. High FFA results in poor biodiesel yield due to soap formation. In the studies carried out by Milano et al [135], Giwa et al [141], Narula et al [143], Adepoju [148], and Kumar et al [149], it was observed that blending of one oil feedstock to another oil decreased the FFA (%) of the mixed oil which resulted to good biodiesel yield (>80 %). The property that affects the biodiesel quality is the acid value which controls the corrosion of engine parts. The acid value of oil feedstock should be below 2 mg KOH/g for the transesterification process [126]. The mixed oil that exceeds the limited range of acid value will be required to undergo an esterification process to reduce the acid value to less than 2 mg KOH/g. However, in the works carried out by Fadhil et al [121,136,137], it was seen that mixing of suitable oils reduces the acid value that can help to reduce the cost and time needed to undergo esterification reaction. In addition to that, high acid values also result in increasing the high heating value (HHV), water content, and kinematic viscosity, but reduce the carbon residue and specific gravity of biodiesel [150]. In similar studies carried out by Mujtaba et al [126], and Mat et al [146], it has been reported that the blending of different oils reduced the density and viscosity indicating an increase in the long-term of fuel engine injection components and performances. From Table 3, it was observed that high viscosities corresponded to low cold flow properties. Iodine value which constitutes for the degree of unsaturation was noticed that the iodine value of the mixed oil was equivalent to the parent feedstocks.

7. Catalysts for biodiesel synthesis from mixed oils

Transesterification is the most frequent and convenient used method for the synthesis of biodiesel, where the oil is allowed to react with short-chain alcohol in presence of the catalyst. The types of catalysts for the reaction are enzymes, homogeneous bases, homogeneous acids, heterogeneous acids, and heterogeneous bases. Enzymes are considered the green catalyst for biodiesel synthesis. *Thermomyces lanuginosus* [151], *C. antarctica* lipase B [152], and *Clostridium* sp [153], are some of the reported enzyme catalysts in biodiesel synthesis. Enzyme catalysts are

considered efficient as they are insensitive to FFAs, do not form soap during the reaction, and require a simple procedure for purification. However, the high cost of enzyme and requirement of a long reaction time are the disadvantages of enzyme-catalyzed reaction, which make it a non-feasible method for cost-effective biodiesel production. Homogeneous base catalysts can produce high yields and convert oil to biodiesel at a very fast rate. H_2SO_4 , CH_3OK , $NaOH$, KOH , and CH_3ONa are the most commonly used homogeneous catalysts [154]. CH_3OK and CH_3ONa are reported to show better results than the rest of the catalysts [155]. However, the use of homogeneous catalysts accounts for various demerits such as the processing issue of generated large waste-water and issues of the neutralization of catalyst [156]. Heterogeneous catalysts are reusable and purification of the product is easy, and also they have very little waste-water production [157]. Heterogeneous catalysts used for the reactions are the solid base catalyst and solid acid catalyst [158]. It is estimated that the alkali catalyst proceeds faster, requires mild reaction conditions, and has high catalytic activity than the acid catalyst [159,160]. Researchers are now concentrating on developing the catalyst for biodiesel synthesis that is cheap, available, eco-friendly, and reusable. Recently, the work is diverted to waste-biomass including agro-waste and ash-based heterogeneous catalysts. These catalysts are reported to have carbonates and oxides of alkali and alkaline earth metals that make the materials highly efficient catalysts with good stability [3,161]. Some of the reported solid based heterogeneous catalysts are *M. balbisiana* Colla [162–164], *M. acuminata* (peduncle) [165], *M. paradisiacal* (plantain) peel [166], *M. paradisiaca* plant (trunk, peel and rhizome) [167], *M. 'Gross Michel'* [168], *Carica papaya* [169], Cocoa pod husk [170], *Citrus sinensis* peel [171], *Brassica nigra* [3], sugarcane bagasse [172], waste wood ash [125], egg shell-snail shell-wood ash [148], *Lattorina littorea* and *Mactra coralline* [173], and sea sand [174]. These reported catalysts showed high activity and fast conversion of the oils. Performances of some homogeneous and heterogeneous catalysts in the production of biodiesel from the mixed oils or blended feedstocks [175–185] are summarized in Table 4.

8. Biodiesel synthesis from mixed oil feedstocks

With the intensification of the application of renewable energy resources to safeguard the environment as well as to combat the future energy crisis, the production and usage of biodiesel as a green biofuel is spreading in transport and allied sectors. Utilization of biodiesel in a diesel engine with no or minimal modification is preferred otherwise a huge change in the sector will be in need that will also cost a massive investment. Thus, the synthesis of biodiesel with identical properties to petrodiesel is given emphasis. As biodiesel from a single oil source reveals the less-competency in usage as fuel due to scarcity of feedstocks and other related issues, the research and development on how to overcome the deficiency is continuing and reported from time to time. In this regard, mixing of oil feedstocks in a suitable ratio prior to transesterification is found to be a suitable approach with improved fuel properties. Thus, the mixing of oil feedstock will overcome the shortage of biodiesel feedstocks. Herein, biodiesel production reported from mixed oil feedstocks is listed in Table 4. A flowchart showing the production of biodiesel from various mixed oils using different catalysts is depicted in Fig. 1.

Fadhil et al [121], carried out the transesterification of castor seed oil (CSO) mixed with waste fish oil (WFO). Various proportions of CSO were mixed with WFO (10, 20, 30, 40, and 50 w/w %) to obtain a homogeneous mixture and the physicochemical properties were analyzed to choose the optimal blend. The equivalent proportion is probed to be the optimal blend. The reaction was then carried out using methanol and base catalyst to investigate the optimum reaction conditions (ORCs). It was observed that the ORCs were 0.5 wt % of KOH , 8:1 MTOR, 32 °C temperature, 30 min reaction time, and stirring speed of 600 rpm, which yielded 95.20 % of biodiesel. The 1H -NMR analysis confirmed the conversion of CSO and WFO to biodiesel. The properties of the produced

Table 3
Physicochemical properties of mixed oils

Feedstocks (Single oil and mixed oil)	FFA (%)	Density (g/cm ³)	KV (mm ² /s)	AV (mg KOH/g)	CN	CV (MJ/Kg)	Pour point (°C)	Cloud point (°C)	IV (g I ₂ /100g oil)	SN (mg KOH/g oil)	Flash point (°C)	References
Waste fish oil	-	0.919	23.20	0.7	-	-	6	-	-	-	220	[121]
Castor seed oil	-	0.998	205.11	0.8	-	-	<-10	-	-	-	244	
Mixture (50:50)	-	0.951	39.88	0.51	-	-	-1	-	-	-	217	
Tung oil	-	0.933	97.58	1.41	-	-	-	-	168.71	-	-	[123]
Canola oil	-	0.912	37	0.13	-	-	-	-	113.85	-	-	
Palm oil	-	0.918	39.6	0.61	-	-	-	-	49.42	-	-	
Mixture (20:50:30)	-	0.923	45.59	0.71	-	-	-	-	116.37	-	-	
Pig fat oil	0.425	0.860	23.95	0.85	59.81	-	-15	-5	-	-	205	[125]
Neem seed oil	7.33	0.890	24.80	14.66	46.33	-	-15	-5	-	-	207	
Mixture (40:60)	2.05	0.852	21.50	4.10	45.83	-	-15	-5	-	-	208	
Thumba oil	5.63	0.880	35	11.25	-	-	-	-	-	184.0	-	[128]
Karanja oil	2.8	0.840	30.7	5.61	-	-	-	-	-	179.5	-	
Linseed oil	0.8	0.890	33.1	1.60	-	-	-	-	-	194.3	-	
Palm oil	0.55	0.900	29.6	1.10	-	-	-	-	-	197.0	-	
Mixture (75:25:75:25)	7.84	0.85	33.0	15.68	-	-	-	-	-	196.3	-	
Rubber seed oil	29.37	0.920	58.11	58.45	47.6	39.32	-	-	112.26	205.47	-	[129]
Neem oil	6.54	0.941	124.43	13.01	57.71	40.82	-	-	84.93	178.86	-	
Mixture (40:60)	-	0.931	95.57	35.34	-	40.25	-	-	96.64	188.64	-	
WCO	-	0.9027	49.05	2.30	-	38.59	-	-	-	-	-	[130]
<i>C. inophyllum</i> oil	-	0.9275	65.48	63.05	-	37.16	-	-	-	-	-	
Mixture (70:30)	-	0.9105	54.12	19.75	-	37.29	-	-	-	-	-	
Castor oil	-	0.965	6.6	0.64	-	40.83	-	-	-	182	-	[131]
Karanja oil	-	0.9308	41.71	14.71	-	41.83	5	15	-	-	240	
Mixture (50:50)	-	0.9447	42.29	15.27	-	35.25	-8	13	-	177.76	250	
<i>Ceiba pentandra</i> oil	-	0.921	34.59	20.23	-	39.49	-3	-7	-	-	282.5	[132]
<i>Nigella sativa</i> oil	-	0.924	32.37	30.35	-	39.25	-7	7	-	-	150.5	
Mixture (50:50)	-	0.923	33.38	25.42	-	39.37	-2	-4	-	-	184.5	
Jatropha oil	-	0.920	37.28	16.68	21	38.96	-	-	-	-	211.7	[133]
Karanja oil	-	0.925	39.9	17.2	32	35.92	-	-	-	-	222	
Cotton seed oil	-	0.922	34.79	27.48	36.5	39.5	-	-	-	-	222	
Mixture (30:30:40)	-	0.902	31.59	4.69	45.71	-	-	-	65	-	220.2	
Jatropha oil	-	0.920	37.28	16.68	21	38.96	-	-	-	-	211.7	[133]
Karanja oil	-	0.925	39.9	17.2	32	35.92	-	-	-	-	222	
Palm oil	-	0.897	40	1.4	41	-	-	-	-	-	257	
Coconut oil	-	0.914	27	0.9	52	-	-	-	-	-	264	
Mixture (20:20:30:30)	-	0.908	30	3.98	38	-	-	-	56	-	210	
<i>C. inophyllum</i> oil	-	0.910	38.22	35.77	-	-	-	-	-	-	-	[134]
<i>Ceiba pentandra</i> oil	-	0.908	28.97	15.38	-	-	-	-	-	-	-	
Mixture (40:60)	-	0.903	25.33	16.66	-	-	-	-	-	-	-	
Palm oil	-	0.914	38.82	4.16	-	38.88	-	-	-	-	-	[126]
Sesame oil	-	0.922	33.11	1.96	-	38.92	-	-	-	-	-	
Mixture (50:50)	-	0.918	37.20	2.78	-	38.79	-	-	-	-	-	
WCO	1.10	0.902	49.05	2.19	-	-	-	-	-	-	-	[135]
<i>C. inophyllum</i> oil	31.78	0.927	65.48	63.25	-	-	-	-	-	-	-	
Mixture(70:30)	9.92	0.910	54.12	19.75	-	-	-	-	-	-	-	
WCO	1.10	0.902	49.05	2.19	-	-	-	-	-	-	-	[135]
Jatropha oil	20.35	0.901	37.13	40.49	-	-	-	-	-	-	-	
Mixture (70:30)	6.66	0.902	47.09	13.26	-	-	-	-	-	-	-	
WCO	1.10	0.902	49.05	2.19	-	-	-	-	-	-	-	[135]
<i>Sterculia foetida</i> oil	4.03	0.912	58.08	8.02	-	-	-	-	-	-	-	
Mixture (70:30)	2.02	0.905	53.07	4.01	-	-	-	-	-	-	-	
WCO	1.10	0.902	49.05	2.19	-	-	-	-	-	-	-	[135]
<i>Ceiba pentandra</i> oil	13.22	0.905	38.64	26.3	-	-	-	-	-	-	-	
Mixture (70:30)	4.62	0.904	47.6	9.2	-	-	-	-	-	-	-	
Castor beans oil	-	0.963	210	0.85	-	-	-20	-3	83	-	205	[136]
Waste chicken oil	-	0.923	20.45	2.0	-	-	-1	13	117.47	-	280	
Mixture (50:50)	-	0.930	49.60	0.92	-	-	0	23	79.12	-	285	
Radish seed oil	-	0.919	19.77	2.01	-	-	-3	-	-	-	802	[137]
<i>Prunus armeniaca</i> oil	-	0.916	26.22	0.68	-	-	-8	-	-	-	189	
Mixture (50:50)	-	0.915	22.91	1.10	-	-	-5	-	-	-	225	
Jatropha curcas	-	0.913	26.61	20.16	-	38.59	-	-	-	-	-	[138]
<i>Ceiba pentandra</i> oil	-	0.905	34.45	16.8	-	38.25	-	-	-	-	-	
Mixture (50:50)	-	0.908	27.22	15.82	-	38.23	-	-	-	-	-	
<i>C. inophyllum</i> oil	-	0.920	55.99	55.64	-	-	-	-	-	-	190	[139]
Palm oil	-	0.890	43.28	0.35	-	-	-	-	-	-	280	
Mixture (50:50)	-	0.910	49.64	27.9	-	-	-	-	-	-	175	
<i>C. inophyllum</i> oil	-	0.929	59.3	65	-	-	-	-	-	382	-	[140]
WCO	-	0.918	26.0	0.25	-	-	-	-	-	193	-	
Mixture (50:50)	-	0.922	40.6	33.4	-	-	-	-	-	292	-	

(continued on next page)

Table 3 (continued)

Feedstocks (Single oil and mixed oil)	FFA (%)	Density (g/cm ³)	KV (mm ² /s)	AV (mg KOH/g)	CN	CV (MJ/Kg)	Pour point (°C)	Cloud point (°C)	IV (g I ₂ /100g oil)	SN (mg KOH/g oil)	Flash point (°C)	References
Palm kernel oil	0.097	0.924	29.07	0.194	-	-	-	-	0.1790	-	-	[141]
Groundnut oil	1.31	0.902	32.66	2.61	-	-	-	-	0.8946	-	-	
Mixture (50:50)	0.17	0.910	31.62	1.42	-	-	-	-	0.5381	-	-	
Hazelnut oil	-	0.872	4.51	-	53.35	-17	-11	168	80.45	-	-	[142]
Sunflower oil	-	0.882	4.04	-	51.25	-16	-14	179	86.25	-	-	
Mixture (50:50)	-	0.875	4.57	-	52.67	-18	-13	174	83.2	-	-	
Jatropha oil	22	0.924	34	-	-	-	-	-	-	-	272	[143]
Algae oil mixture	0.5	0.860	21	-	-	-	-	-	-	-	-	
Mahua oil	1	-	-	-	-	-	-	-	-	-	-	
Simarouba oil	-	-	-	-	-	-	-	-	-	-	-	[144]
Mixture (50:50)	-	0.912	43.94	14.38	-	36.04	14.20	-	-	-	242	
Sunflower oil	-	0.915	49.56	-	-	-	-	-	-	-	-	[145]
Castor oil	-	0.957	610.74	-	-	-	-	-	-	-	-	
Mixture (80:20)	-	0.920	70.82	-	-	-	-	-	-	-	-	
Refined palm oil	-	0.904	42	7.28	-	40.3	-	-	-	-	210	[146]
Melaleuca cajuputi oil	-	0.869	0.2	5.52	-	43.2	-	-	-	-	50	
Mixture (32:68)	-	0.881	5.9	-	-	-	-	-	-	-	-	
WCO	0.73	0.874	32.94	1.46	-	-	-	-	-	-	-	[147]
Honne seed oil	17.48	0.903	43.93	34.79	-	-	-	-	-	-	-	
Mixture (70:30)	6.14	0.883	43.70	12.21	-	-	-	-	-	-	-	

FFA – Free fatty acids, KV – Kinematic viscosity, AV – Acid value, CN – Cetane number, CV – Calorific value, IV – Iodine value, SN – Saponification number.

fuel (kinematic viscosity, flash point, pour point, and density) were found as per the ASTM D6751 standard.

Issariyakul et al [124]. studied the performance of biodiesel obtained from a mixture of canola oil (CO) and WCO. They carried out the reactions using varying proportions of oil mixtures (80:20, 60:40, 40:60, 20:80 ratio of WCO and CO) using methanol and ethanol in the ratio of 6:1 to the oil, KOH (1 wt % of oil) as the catalyst for 2 h and at the speed of 600 rpm. HPLC chromatograms of canola methyl esters reported the conversion of triglyceride to esters, but that of waste cooking methyl esters reported the incomplete conversion due to saponification. However, the ester percentage (both in methyl and ethyl) increased with the increase of canola oil percentage in the oil mixture thereby improving the biodiesel yield. They also found that the acyl-glycerol of ester percentage increased with increasing WCO percentage in the feedstock mixture which indicates the high acid value and fatty acid content of WCO. The FFA content, water content, acid value, heating value, density, and viscosity of the esters were also analyzed. The water content and density of the esters met the ASTM standard. However, the acid value and viscosity of ethyl esters did not meet the desired limit of 0.5 mg KOH/g and 1.9-6.0 mm²/s, respectively. They reported that the boiling points of ethyl esters were higher than the methyl esters due to high molecular weight. Methanolysis of equivalent proportions of oil mixture gave satisfactory yield, but ethanolysis gave poor yield. However, increasing the amount of CO (60 %) in comparison to WCO (40 %) increased the amount of biodiesel. Thus, the addition of CO increased the biodiesel yield.

Biodiesel from the blend of pig fat oil (PO) and neem oil (NO) was synthesized by Adepoju [125] using CaO based catalyst derived from the mixture of palm kernel shell husk and fermented kola nut husk. The catalyst was calcined at 800°C for 3 h in a muffle furnace at standard atmospheric pressure. Varying blends of NO-PO (v/v) were prepared (10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10). Central composite design (CCD) was implemented to investigate the transesterification parameters. Blend of NO (60):PO (40) was chosen as the optimal blend as it showed low viscosity. The optimum predicted biodiesel yield was 98.05 wt % at 2.179 g of catalyst load, 5.9:1 MTOR, 57.45 min of reaction time, and reaction temperature of 59.91 °C. Elemental analysis of the catalyst showed the presence of CaO as a predominant component. The predicted values were validated in triplicate and the average biodiesel yield of 98.03 wt % was reported. Physicochemical properties of the biodiesel were found within standard

limits.

Mujtaba et al [126]. produced palm-sesame biodiesel using ultrasound-assisted transesterification reaction. They optimized the process parameters using the response surface methodology (RSM) tool based on the Box-Behnken design (BBD) and extreme learning machine (ELM) modeling coupled with the cuckoo search algorithm. The homogeneous oil mixture of palm oil and sesame oil was achieved by mixing in varying proportions at 60°C for 2 h. The oil mixture was characterized and an oil mixture of 50 wt % palm oil and 50 wt % of sesame oil gave the best result in acid value, kinematic viscosity, and calorific value, and was chosen for the study. The respective methyl esters of individual oil and the oil mixture were prepared via an ultrasound-assisted process using KOH as the catalyst. They reported that the ELM model predicted the palm-sesame methyl esters more accurately. The ORCs were recorded to be 38.96 min of reaction time, MTOR to be 60 %, catalyst load of 0.70 % w/w, and biodiesel yield of 96.6138 % was achieved. The physicochemical parameters of the methyl esters were estimated and were found to be in accordance with biodiesel standards.

Hong et al [127]. investigated fuel properties of canola-lard mixed oil biodiesel on account of the number of double bonds and molecular weight. The biodiesel was produced from a mixture (9:1-1:9) of canola oil and lard using methanol and ethanol. The reaction was carried out via esterification using H₂SO₄ as the catalyst. High heating value (HHV) and oxidative stability (OS) are considered based on molecular weight and number of double bonds in fatty acid alkyl ester (FAAE). They stated that HHV increases with increasing molecular weight but decreases with the increasing number of the double bond of FAAE. However, OS decreases with increasing molecular weight but increases with the number of double bonds of FAAE. ATOR was dependent on the molar ratio of mixed oil (canola oil to lard). They reported that for 50 wt % of canola oil, the ATOR was 9, and for <50 % of canola oil content, the ATOR was 12. The HHV was similar for varying ratios of oil mixtures, but higher proportions of lard contributed to OS which satisfied the biodiesel standards.

Gupta et al [128]. synthesized biodiesel from the mixture of edible and non-edible oils using KOH as the catalyst. Thumba oil, karanja oil, linseed oil, and palm oil were blended in various proportions and chosen for a two-step reaction due to high FFA content. Esterification was done using H₂SO₄ and transesterification was done using KOH as the catalyst. Optimum variables were investigated by RSM. Maximum yield of

Table 4
The performances of different catalysts used in biodiesel production from mixed (blended) oils

Biodiesel feedstocks (Mixed or blended oil)	Catalyst	Parameters Catalyst load (wt %)	Alcohol/oil	Temp (°C)	Time (min)	Yield (%)	References
Castor seed oil and waste fish oil	KOH	0.50	8:1	32	30	95.20	[121]
Tung oil, canola oil and palm oil	KOH	2	6:1	25	5	98.33	[123]
WCO and canola oil	KOH	1	6:1	50	120	-	[124]
Pig fat oil and neem oil	Palm kernel shell husk and fermented kola nut husk	2.179	5.9:1	59.91	57.45	98.05	[125]
Palm oil and sesame oil	KOH	0.7	60 (V/V%)	60	38.96	96.61	[126]
Canola oil and lard	KOH	1	9:1 (Methanol)	55	60	96.6	[127]
Canola oil and Lard	KOH	1	9:1 (Ethanol)	65	80	96.8	[127]
Thumba oil, karanja oil, linseed oil and palm oil	KOH	1.9 g/100 cc feed	8.8:1	43.50	58.4	98	[128]
Neem oil and rubber seed oil	<i>Enterolobium cyclocarpum</i> pod husk	2.96	11.44:1	65	5.88	98.77	[129]
WCO and <i>Calophyllum inophyllum</i> oil	KOH	0.774	59.60 (V/V%)	60	7.15	97.40	[130]
Castor oil and karanja oil	Enzyme (lipase)	10 % (v/v)	6:1	50	1440	~78	[131]
<i>Ceiba pentandra</i> and <i>Nigella sativa</i> oil	KOH	1	4:1	60	120	-	[132]
Jatropha oil, karanja oil and cotton seed oil	KOH	1	4:1	60	120	-	[133]
Jatropha oil, karanja oil, palm oil and coconut oil	KOH	1	4:1	60	120	-	[133]
<i>Calophyllum inophyllum</i> and <i>Ceiba pentandra</i> oils	KOH	0.78	37%	60	153	95.18	[134]
WCO and <i>Calophyllum inophyllum</i> oil	KOH	0.5	60 (V/V)%	55	90	96.84	[135]
Castor bean oil and WCO	KOH	0.75%	8:1	60	30	97.20	[136]
Radish oil and apricot kernel oil	KOH	0.75	6:1 (Methanol)	60	45	96.12	[137]
Radish oil and apricot kernel oil	KOH	0.75	6:1 (Methanol and Ethanol)	60	45	94.23	[137]
Radish oil and apricot kernel oil	KOH	1	8:1 (Ethanol)	65	75	95.19	[137]
<i>Jatropha curcas</i> and <i>Ceiba pentandra</i> oils	KOH	0.5	30%	60	120	93.33	[138]
<i>Calophyllum inophyllum</i> and palm oils	KOH	0.5	12:1	60	90	-	[139]
<i>Calophyllum inophyllum</i> oil and WCO	<i>Donax deltooides</i> shell	7.5	63.8 (V/V)%	65	129.3	96.5	[140]
Palm kernel oil and groundnut oil	NaOH	1	6:1	60	60	86.56	[141]
Hazelnut oil and sunflower oil	KOH	0.7	6:1	60 ± 0.5	120	97.9	[142]
Jatropha oil and algae oil	KOH	0.9	3:5	50	180	81.98	[143]
Mahua oil and simarouba oil	KOH	3.5	5:1	60	30	98	[144]
Sunflower oil and castor oil	KOH	5.4	21:1	60	3	88.4	[145]
WCO and honne seed oil	<i>E. cyclocarpum</i>	1.75	6:1	-	4	100	[147]
<i>Iringia gabonensis</i> , <i>Pentaclethra macrophylla</i> , and <i>Elaeis guineensis</i> oil	Wood ash, snail and eggshells	4.5	8:1	61.61	64.71	98.00	[148]
<i>Carica papaya</i> , <i>Citrus sinensis</i> , <i>Hibiscus sabdariffa</i> seeds, and waste used oils	<i>Lattorina littorea</i> and <i>Maetra coralline</i>	3	6:1	70	60	99.95	[173]
Safflower oil, soybean oil and WCO	Sea sand	7.5%	12:1	60	360	95.4	[174]
<i>Annona muricata</i> and <i>Calophyllum inophyllum</i> oil	Waste wood ash	0.39	-0.78	0.92	0.89	99.1498	[175]
<i>Jatropha curcas</i> oil, castor oil and WCO	KI impregnated zinc oxide	7	11.68:1	59	59	92.35	[176]
Waste sunflower oil palm oil, gingili oil, castor oil, and ground nut oil	Al(HSO ₄) ₃	0.5	16:1	220	50	81	[177]
Oleic acid and refined cottonseed oil	SO ₄ ²⁻ /TiO ₂ -SiO ₂	3	9:1	200	360	92	[178]
Beef tallow and soybean oil	<i>Thermomyces lanuginosus</i>	1.45%	4.5:1	35	480	79.9	[179]
WCO and refined palm oil	Fly ash	13.57	6:7	55	120	73.8	[180]
Different WCOs	KOH	0.75	8:1	50	80	90	[181]
<i>Jatropha curcas</i> oil and waste food oil	KOH	1	6:1	50	120	97.1	[182]
Waste fish oil, bitter almond oil, and WCO	Lithium impregnated waste tires derived activated carbon	3	9:1	40	60	92.23	[183]
Waste frying oil and palm oil	KOH	1	6:1	60	120	98.65	[184]
Sunflower and soybean oils	NaOH	0.6	19:1-21:1 (V/V%)	60	60	93.5	[185]
Waste fish oil and palm oil	KOH	0.5	9:1	60	60	98.5	[186]
Pongamia and neem oils	NaOH	0.67	6:1	60-65	77	86.2	[187]
<i>Sterculia foetida</i> and rice bran oil	KOH	0.7	42%	-	50.64	98.93	[188]
Chicken fat and WCO	K-based chicken bone composite	4	6:1	60	120	97.44	[189]

biodiesel was obtained for optimum blend of 25 mL of karanja oil + 75 mL of linseed oil + 25 mL of palm oil + 75 mL of thumba oil. The ORCs for the said blend were temperature of 43.50°C, MTOR of 8.8:1, 1.9 g of catalyst load, and reaction time of 58.4 min. The optimization model was satisfactory as it revealed a reliable determination of coefficient (R² 0.96). Response surface plots were taken by the design of expert software and revealed that the FAME yield increased with increasing temperature, alcohol content, and reaction time.

Microwave irradiation-assisted transesterification was carried out by Falowo et al [129]. to produce biodiesel from the blends of neem oil (NO) and rubber seed oil (RSO) using the catalyst obtained from

Enterolobium cyclocarpum pod husk. Maximum biodiesel yield was investigated using a central composite rotatable design (CCRD) coupled with RSM. Different blends of NO:RSO were prepared (100:0, 80:20, 60:40, 50:50, 40:60, 20:80, 0:100). A two-step reaction was carried out for an oil blend of 60 % NO and 40 % RSO as this blend had favorable properties in comparison to other blends. Esterification was done using (Fe₂SO₄)₃.xH₂O as a catalyst. The esterified oil blend was transesterified using the calcined catalyst (700°C, 4 h) and methanol. The ORCs suggested by RSM were catalyst dosage of 2.96 wt %, a reaction time of 5.8 min, MTOR of 11.44:1, and microwave heating of 150 W, and biodiesel yield obtained was 99.61 %. These predicted values were triplicate

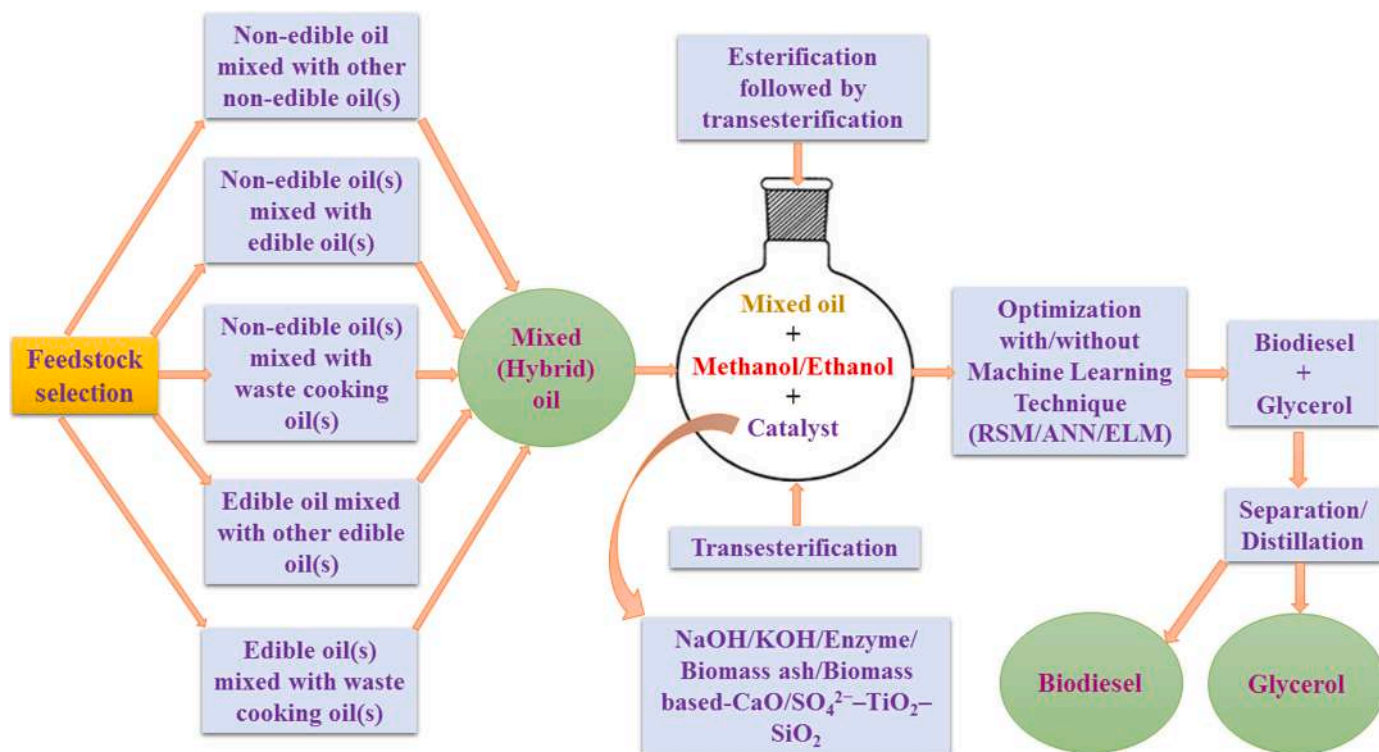


Fig. 1. A flowchart showing the production of biodiesel from various mixed oils using different catalysts.

validated and revealed the average biodiesel yield as 98.77 ± 0.16 %. The properties of the fuel produced were under the standard limits.

In another study, Milano and co-workers [130] adopted microwave irradiation-assisted transesterification for biodiesel synthesis from the mixture of *Calophyllum inophyllum* oil (CIO) and WCO (30:70). They recorded high FFA content of the blended oil (9.92 %) and hence they degummed using 5 % of dilute ortho-phosphoric acid for 30 min at 60°C followed by esterification with methanol and H_2SO_4 as a catalyst. The esterified oil was later transesterified using KOH as a catalyst. They optimized the reaction using RSM based BBD and predicted the biodiesel yield by quadratic response surface regression model. They observed that the ORCs were 59.60 (v/v) % of MTOR, 0.774 (w/w) % of catalyst loading, 7.15 min of reaction time, and 60°C of reaction temperature and the yield of biodiesel was found to be 97.40 %. The oxidation stability of biodiesel was very high (18.03 h) which was attributed to the high polyunsaturated fatty acid content of the oil blend. They further produced biodiesel from the conventional transesterification method and found that the methyl esters yield from the same oil blend was very low (89.15 %) compared to that from the microwave irradiation-assisted method. Hence, they concluded that microwave irradiation was effective for the transesterification process.

Kumar et al [131]. studied lipase-catalyzed transesterification of the mixture of non-edible oils (karanja and castor) in equal proportions with 2-propanol using sodium alginate and polyvinyl alcohol (PVA) based bio-support beads immobilized lipase catalyst. They recorded ~78 % of biodiesel yield under the ORCs of 6:1 of 2-propanol to oil molar ratio, 24 h of reaction time, 10 % (v/v) of lipase loading, and 50 ± 1 °C of reaction temperature. The physicochemical properties of the mixed oil biodiesel were under ASTM D6751 and EN14214 standards. FT-IR and 1H -NMR analyses showed the conversion of mixed oil to fatty acid propyl esters.

Khan et al [132]. synthesized biodiesel from *Ceiba pentandra* and *Nigella sativa* oils, and the mixture of oils. The synthesis was carried out via a two-step process. Acid-catalyzed esterification was done using MTOR of 2:1 and H_2SO_4 for 3 h at 60°C with a stirring speed of 700 rpm. The esterified oil was mixed and transesterified using 1 wt % KOH at 60°C with a stirring speed of 700 rpm for 2 h. Palmitic acid, linoleic acid,

and oleic acid were the main constituents of the produced biodiesel. Physicochemical properties of biodiesel were analyzed and found within the ASTM D6751 standard. They further blended the biodiesel with diesel and found out that an increase in the percentage of biodiesel increases the quality of physicochemical properties.

Sharma et al [133]. prepared two samples of bio-mix methyl esters (BMME) from the ternary and quaternary mixture of raw oil feedstocks to study the effect on FAME profile and fuel property. JCO, karanja, cotton, palm, and coconut oils were the five selected oils that were mixed to obtain raw bio-mix oil (RBMO) sample. The quaternary mixture (BMME-2) was prepared by the mixture of JCO, karanja, palm, and coconut oils. However, the ternary mixture (BMME-1) was prepared from JCO, karanja, and cotton oils. The mixtures were firstly esterified using H_2SO_4 with 6:1 MTOR at a temperature of 60°C for 3 h with a stirring speed of 600 rpm. The product was then transesterified with 4:1 MTOR, and KOH as an alkaline catalyst at 60°C for 2 h with 600 rpm of stirring speed. GC-MS analysis revealed that the saturated fatty acid percentage (SFA %) for bio-mix methyl ester increased, whereas unsaturated fatty acid percentage (USFA %) decreased. It was also observed that the SFA level of BMME-1 was higher than that of BMME-2. The fuel properties of BMME were found within the biodiesel standard.

Ong et al [134]. transesterified the mixture of CIO and *Ceiba pentandra* oil by a novel modeling approach of Artificial Neural Network (ANN) coupled with Ant Colony Algorithm (ACO). The oil mixture was achieved by mixing CIO and *Ceiba pentandra* oil (CPO) in different ratios (20:80, 40:60, 60:40, and 80:20 wt %). The optimal blend (CIO:CPO, 40:60) was transesterified via the ANN-ACO model, which predicted the ORCs that were 37% of MTOR, 0.78 wt % of KOH, 153 min reaction time, 60°C temperature, and stirring speed of 1000 rpm. At these conditions, 95.87 % yield of biodiesel was achieved. The fuel properties were determined and found in accordance with ASTM and EN standards. In the study, they concluded that the ANN-ACO model is simple and reliable in comparison to other optimization tools.

Milano and co-workers [135] proposed a scheme that could convert the waste edible oil to biodiesel. Though the waste oil contains a lot of fatty acid and impurities, they successfully converted the waste edible

oil to biodiesel. In the work, they blended 70 vol % of WCO with CIO, and the results are shown in Table 4. In order to remove all the fatty acid contents and the impurities, they conducted the reaction in three stages. Firstly, they did the degumming of the waste oil. Secondly, the esterification was done and at last transesterification for the synthesis of biodiesel. During the transesterification, all the parameters like temperature, MTOR, catalyst dose, and reaction time were maintained (Table 4). The properties resemble the fuel specification specified in ASTM D6751 and EN 14214 standards.

Fadhil and Ahmed [136] did transesterification of the mixture of waste chicken oil and castor bean oil using KOH as a catalyst. Different blends of castor bean oil and waste chicken oil (10, 20, 30, 40, and 50 % w/w) were prepared. Blend of equal proportion was found to be optimum with the acid value of 0.92 mg KOH/g oil and 0.46 % FFA content. The ORCs were 0.75 % (w/w of oil) catalyst concentration, MTOR 8:1, 60°C, 30 min reaction time, and 600 rpm. The biodiesel yield was found to be 97.2 %. A kinetic study was done via a pseudo first-order kinetic model that showed the activation energy of 8.85 kJ mol⁻¹. The biodiesel was also blended with petroleum diesel and showed that the density, kinetic study, pour point and flash point increased with the increasing percentage of biodiesel and were under the ASTM standard.

Fadhil et al [137], studied the characteristics of biodiesel produced via transesterification of a mixture of apricot kernel oil (AKO) and radish oil (RO). The reaction was carried out in equal proportions of RO-AKO blend with ethanol, methanol, and mixed methanol/ethanol to produce methyl biodiesel (MBD), ethyl biodiesel (EBD), and methyl/ethyl biodiesel (MEBD) respectively, using KOH as the catalyst. A refining media (activated carbon) was prepared from ZnCl₂ activation of apricot shells which was found to be an efficient adsorbent due to its high surface area. The transformation of RO-AKO to biodiesel was confirmed by FT-IR and ¹H-NMR analyses. They observed that RO-AKO conversion to MBD and MEBD was maximum at 60°C temperature, KOH concentration of 0.75 % (w/w of oil), and 45 min of reaction time, whereas for conversion to EBD, the conditions were 65°C, 1 % (w/w of oil) and 75 min, respectively. High ester contents were observed for MBD and MEBD than that of EBD (Table 4). The activation energy for the kinetic study of methanolysis of RO-AKO was found to be 27.27 kJ mol⁻¹. They further blended the biodiesel with petroleum diesel and observed that the flash point, density, kinematic viscosity, and pour point increased with increased biodiesel percentage in the blend.

Optimization of biodiesel from the mixture of *J. curcas* oil and *C. pentandra* oil was studied by Dharma et al [138], using RSM-based BBD tool. Five different proportions of oil were blended, among which 50:50 blend was chosen. Esterification of the oil blend was done using H₂SO₄ (1 % v/v), 30 % of MTOR and at 60 °C for 3 h. This was followed by transesterification producing 93.33 % FAME at the ORCs of 30% of MTOR, 0.5 wt % of KOH concentration, and 2 h of reaction time at 60 °C. They reported 72.9 % and 24.2 % of total unsaturated and saturated fatty acid contents respectively in the produced biodiesel.

Damanik et al [139], investigated the biodiesel synthesized from the mixture of CIO and palm oil of equivalent ratio. The oils were first degummed individually and then esterified using H₂SO₄, followed by transesterification using KOH. The fuel property of the produced biodiesel was estimated as per EN 14214 and ASTM D6751 standards. They reported that the oxidation stability (OS) was very high (114.2 h) due to high unsaturation in biodiesel. They also reported that the biodiesel had a density of 880 kg/m³, kinematic viscosity of 4.5 mm²/s, and acid value of 0.4 mg KOH/g.

Niju et al [140], studied the utility of *Donax deltoideis* shells as the heterogeneous base catalyst for the conversion of CIO and WCO mixture (1:1) to methyl esters. They optimized the reaction parameters using RSM based on CCD that revealed 7.5 wt % of catalyst load, 63.8 (v/v) % MTOR, 129.3 min of reaction time, and 65°C of reaction temperature. The maximum biodiesel conversion from the ORCs was reported to be 96.5 % which was confirmed by ¹H-NMR analysis.

Giwa and co-workers [141] reported a method to produce biodiesel

(Hybrid oil methyl esters, HOME) from hybrid oils. In the work, they took the combination of kernel palm oil (KPO) and groundnut oil (GNO). They found that KPO was highly saturated with a medium carbon chain, whereas GNO was found to be highly unsaturated and contained a long carbon chain. After investigating the fatty acid contents, they blended both the oils in the ratio of 50:50 (v/v). The fatty acid components in hybrid oil were found to be 35.62 % oleic acid, 24.23% lauric acid with 47.80 % saturated fatty acid, and 52.26 % unsaturated fatty acid. The kinematic viscosity of HOME was found to be 3.69 mm²/s and this value was found to be very low compared to the other biodiesel from the literature. This comparatively low value suggested that they are accessible or quite easy to flow, atomization and fully ignite in terms of combustion. They concluded that the oil blends can improve the properties of biodiesel.

The quality of biodiesel from hazelnut kernel oil, sunflower oil, and hybrid oil (50:50 v/v) was studied by Saydut et al [142]. The transesterification was carried out for individual oils and hybrid oil using 6:1 ATOR, 0.7 % of KOH at 60 ± 5°C for 2 h. They recorded 97.5 %, 97.3 %, and 97.9 % conversions for hazelnut kernel oil, sunflower oil, and hybrid oil, respectively. Thus, they concluded that transesterification reaction is not oil selective and dedicated to high ester conversion.

Narula et al [143], investigated the parameters for transesterification of algae oil and JCO blend. KOH concentration of 0-2 % (w/w), the residence time of 60-180 min, MTOR of 20-60 % (v/v) and reaction temperature of 50°C were the reaction conditions. The ORCs were investigated using RSM-based BBD and recorded 81.98 % of biodiesel yield for 3:5 (v/v) of MTOR, 0.9 % (w/w) of KOH concentration, and 180 min of residence time at 50°C.

Jena et al [144], developed a pretreatment process followed by transesterification to obtain biodiesel from the mixture of mahua (M) and simarouba (S) oils containing high FFAs. Pretreatment of FFAs was carried out for various oil mixtures using methanol and H₂SO₄ as an acid catalyst. This was followed by transesterification of the product that contained an acid value of less than 2 ± 0.25 mg KOH/g of oil using KOH as the catalyst, 5:1 ATOR at 60°C reaction temperature. The best optimum parameters were determined by the ANN technique. Oil mixtures in the proportions of 75M:25S, 50M:50S, and 25M:75S were recorded as the best and produced approximately 98 % of biodiesel.

Flow patterns and effects of flow patterns in a milli-channel reactor of transesterified castor oil (CO), sunflower oil (SO), and mixed oil were studied by Jamil et al [145]. Flow patterns were observed by fixed parameters which were MTOR of 21:1, KOH concentration of 5.4 wt %, the residence time of 180 s, and temperature of 60°C. Castor oil had high viscosity, while sunflower oil had low viscosity that showed parallel flow and slug flow throughout. For varying proportions of oil mixtures, they observed slug flow upstream and parallel flow downstream. They observed that the formation of slug slow increased the mass transfer of the reagents thereafter increased the FAME yield. They reported that 20 ml of CO and 80 ml of SO resulted in 88.4 % of FAME.

Falowo et al [147], investigated biodiesel synthesis from a mixture of honne seed oil (HSO) and WCO following a two-step microwave-assisted reaction. The catalysts investigated were KOH, Ba(OH)₂, and calcined material of waste *Enterolobium cyclocarpum*. The optimization of the process was done by Taguchi orthogonal array method. Oil blends of different ratios were prepared for the reactions, which were 70:30, 50:50, 30:70 of WCO:HSO, and among these, 70:30 (WCO:HSO) showed the lowest acid value. The esterification reaction of the selected oil blend using H₂SO₄ was carried out following the Taguchi method to investigate the reaction parameters. Simultaneously, transesterification reaction was carried out using a similar method with the three different catalysts. They observed that esterification reaction resulted in a minimum reduction of FFA under the ORCs which were 30:1 of MTOR, 2 min of reaction time, 150 W of heating power, and 1.5 wt % of H₂SO₄ dosage. In the process, they reported the highest biodiesel yield of 99.81 % at 12:1 MTOR, 4 min of reaction time, 450 W of heating power, and 1 wt % of catalyst dosage. However, biodiesel produced using KOH showed

better quality in terms of acid value.

A catalyst from the ternary mixture of eggshell, snail shell, and wood ash was developed by Adepoju et al [148]. for the conversion of ternary oil mixture of *Irvingia gabonensis* (33 mL), *Pentaclethra macrophylla* (33 mL) and *Elais guineensis* oil (34 mL) to biodiesel. The amount of biodiesel produced was 98% at the reaction conditions of MTOR of 8:1, 4.5 g of catalyst load, 61.61°C of reaction temperature, and 64.71 min of reaction time. However, the predicted optimized biodiesel yield was 97.33 % which is validated in triplicate and the average biodiesel yield was found to be 97.22 %. The high percentage of biodiesel yield was attributed to the fact that the percentage of CaO present in catalyst blend is very high in comparison to a single catalyst. However, the catalytic activity of the catalyst is reduced after 3rd cycle as the active sites of the catalyst surface are interfered with by transitional products.

Adepoju et al [173]. developed a catalyst from a binary mixture of *Lattorina littorea* and *Maetra coralline* for biodiesel production from a quaternary mixture of *Carica papaya* (25 mL), *Citrus sinensis* (25 mL), *Hibiscus sabdariffa* (25 mL), and waste used oil (25 mL). The biodiesel synthesis was optimized by RSM coupled with CCD. They observed that the developed catalyst was effective due to the presence of CaO (99.02 %). They reported the highest yield of 99.68 % biodiesel at a catalyst amount of 2 g, a reaction time of 70 min, ethanol to oil ratio of 7:1 and a reaction temperature of 60°C. They analyzed the biodiesel qualities and were found as per the biodiesel standard.

Adepoju [175] developed a heterogeneous catalyst from waste wood ash to synthesize biodiesel from the oil mixture of *Annona muricata* oil and CIO. They used RSM to investigate the transesterification parameters. The catalyst was calcined at 1100°C for 3 h. They extracted the *Annona muricata* oil and CIO by the Soxhlet extractor using hexane. The oil blend that had the lowest acid value (2.02 mg KOH/g oil) was chosen for the oil conversion. They treated the oil to reduce the acid value of the oil blend (4.10 mg KOH/g) using H₂SO₄ (1.0-3.0 % v/v) as the catalyst under reaction temperature (between 50 and 90°C) and reaction time of 40-80 min. They then transesterified the esterified oil with calcined waste wood ash (2.0 %) catalyst and the results are shown in Table 4. BET and XRD analysis revealed that the decrease of the percentage of CaO after reuse resulted in the decrease of the biodiesel yield.

Malani et al [176]. investigated the transesterification of the non-edible oil mixture using a developed heterogeneous catalyst. They prepared the catalyst (KI impregnated ZnO) by impregnating 75 mL of 35 % (w/w) KI solution to 25 g of ZnO. The oil mixture was pretreated due to high acid value using H₂SO₄ (5 % (w/w)), 1 h of reaction time, and 15:1 of ATOR at 65°C. This was followed by transesterification for different compositions of feedstock which they carried out using 3 % (w/w) of catalyst dosage, and 9:1 ATOR at 60°C. The optimization was done by RSM-based BBD and reported the highest oil conversion of 92.35±1.08 % under ORCs of 7 % (w/w) of catalyst dosage, and 11.68:1 ATOR at 95°C. Thus, they concluded that the non-edible oil mixture was feasible for biodiesel production.

Ramachandran et al [177]. produced biodiesel from the mixture of waste vegetable oils using Al(HSO₄)₃ as a catalyst via the transesterification process. The catalyst was developed by sulfonation of AlCl₃. They achieved the highest conversion of 81 % under ORCs of 16:1 MTOR, 0.5 wt % of catalyst dosage, and 220°C of the reaction temperature in 50 min. They stated that Al(HSO₄)₃ was highly active due to high acid site density and the hydrophilic group that allowed the contact between methanol and carbonyl group. The fuel properties were within the ASTM D6751 and EN14214 standards.

Peng and co-workers [178] synthesized SO₄²⁻/TiO₂-SiO₂ solid acid catalyst that could convert a low-quality feedstock containing high FFA to biodiesel. They probed that the reaction parameters like temperature, ATOR, and the FFA content in the material measure how efficient and purity the synthesized biodiesel results. In the experiment, they observed that reaction at 200°C is the optimum temperature. Similarly, they observed that minimal catalyst concentration (3 wt %) maintained the formation of biodiesel (Table 4). It was mentioned that

SO₄²⁻/TiO₂-SiO₂ solid acid catalyst is cheap, eco-friendly, and very robust for the generation of biodiesel.

Wancura and co-workers [179] reported the activity of biocatalyst, *Thermomyces lanuginosus*, for the substitution influence of degummed soybean oil by deacidified beef tallow and the water content on the FAME production. They evaluated for 0, 25, 50, 75, and 100% of oil substitution by tallow, and 0.0, 3.0, 9.0, 12.0 % of distilled water, under the reaction conditions of 4.5:1 MTOR, 1.45 % of catalyst loading, and 35°C of reaction temperature. They reported that the FAME yield didn't increase after 480 min of reaction time which accounts for the inability of catalyst to stop inhibition due to methanol. The concentration of water with 6 % and 9 % recorded 75 % and 79.9 % of biodiesel yield respectively. They observed that FAME yield was the highest (84.6 %) when beef tallow was used but decreased to 73.1 % when soybean oil was used.

Vargas et al [180]. explored the utility of fly ash as the catalyst for the synthesis of biodiesel from the mixture of refined palm oil and WCO. They prepared the catalyst by drying the fly ash at 120°C for 2 h. The reaction was optimized by RSM and BBD. The highest biodiesel yield of 73.8 % was reported using predicted ORCs of 13.57 wt % of catalyst load, 6.7 of MTOR, 55°C of reaction temperature, and 2 h of reaction time for 28.04 wt % of oil mixture. They reported that reuse of the catalyst was possible as there was no loss in activity and could be used up to three times, but the catalyst must be regenerated by washing followed by calcination.

Phan and Phan [181] experimented by collecting different WCO. They experimented on the laboratory scale just to justify the quality of biodiesel produced. They reported 88–90 % of biodiesel yield with 0.75 wt % KOH using MTOR of 7:1–8:1 at 30–50°C of reaction temperatures. The production efficiency was good when the reaction was conducted for at least 1 h. They observed that the biodiesel produced contains a high carbon residue which is very unhealthy for the environment. The carbon residue of 4.0 wt% for biodiesel was obtained, whereas it was 0.05 wt % for diesel. They observed that mixing biodiesel with diesel drastically decreased the carbon residue and significantly increased the volatility. Eventually, they obtained that a blend of 20 % biodiesel and 80 % diesel (B20) could be applied in diesel engines.

Berchmans and co-workers [182] studied the kinetics of methanolysis of the mixture of JCO and waste food oil using KOH as a catalyst (Table 4). In the work, they observed that more amounts of water and soap were produced and this was due to the neutralization of more amounts of FFA. They could convert the JCO and waste oil mixture into biodiesel by increasing the reaction speed and also by increasing the temperature of the reaction medium. They concluded that the factors like reaction speed, reaction time, and catalyst concentration were the factors to be considered to get 97.1 % biodiesel.

Ayoob and Fadhil [183] studied the influence of Li-supported waste tires derived activated carbon (WTAC) as a base catalyst for the synthesis of biodiesel from non-edible oils. The catalyst was characterized by different techniques after which 40 Li/WTAC was selected as an optimum catalyst due to its high catalytic performance that produced 92.23 ± 2.0 % of biodiesel. The ORCs were recorded as 9:1 as MTOR, 3 wt % of catalyst dosage, 1 h of reaction time, and 40°C of reaction temperature. The catalyst could be reused up to 4 times as the leaching of the catalyst was ineffective. The kinetic model demonstrated pseudo first-order with a rate constant of 0.0405 min⁻¹ at 40°C and activation energy of 19.01 kJ/mol.

Alarcon et al [184]. tried to establish waste frying oil (WFO) as a biodiesel feedstock. The FFA content of WFO was very high and hence, they mixed WFO with virgin palm oil (PO) in 6 different proportions (0:100, 5:95, 10:90, 15:85, 20:80, 100:0 of WFO:PO). The reaction was carried out via transesterification method using KOH as a catalyst, MTOR of 6:1, reaction temperature of 60°C, and reaction time of 2 h. They found that when 95 % of PO was employed to the 5 % of WFO, the maximum biodiesel yield of 98.69 % was obtained. They analyzed the properties of biodiesel and were found within the standard limits.

Elkelawy et al [185]. studied the performance of engine and emission properties of diesel mixed with biodiesel produced from the blend of edible oils (1:1 of soybean oil and sunflower oil). The biodiesel was prepared via transesterification using NaOH as the catalyst, MTOR of 20 v/v %, and 500 rpm of stirring speed at 60 °C in 1 h. The biodiesel yield was found to be 93.5 %. The obtained biodiesel was then mixed with pure diesel and combustion characteristics were recorded based on one thousand cycles of three different ratios (70:30, 50:50, 30:70 % of diesel and biodiesel). CO, CO₂, NO_x, O₂, and HC were analyzed by an automotive emission analyzer and reported that CO, HC, CO₂, exhaust gas, and smoke reduced on increasing the biodiesel percentage. However, exhaust oxygen (EO) and NO_x increased as the biodiesel has oxygen content.

Almeida et al [186]. studied the conversion characteristics of waste fish oil, palm oil, and waste frying oil mixture to biodiesel. The individual oil and mixed feedstock were optimized by RSM. The biodiesel obtained from individual feedstock was about 82-92 %. However, the biodiesel obtained from the mixture of two oils was high enough. The highest FAME yield of 98.5 % was obtained for 33.3:66.7 of waste fish oil and palm oil at the reaction parameters of 0.5 wt % of NaOH and 9:1 of MTOR at 60°C in 1 h. They reported that the difference in the FAME yield was due to the difference in polyunsaturated fatty acids and monounsaturated fatty acids.

Vinayaka et al [187]. synthesized biodiesel from a mixture of non-edible oils (pongamia and neem oils) via transesterification process using NaOH (0.7-1.3 % w/w), methanol 6-12 molar ratio and temperature maintained in the range of 60-65°C. The reaction parameters were optimized using RSM-based CCD. The FFAs content of the oil mixture was 3.5 % and hence, it was esterified to reduce the FFAs content. The esterified oil was then transesterified. RSM revealed the ORCs and these were reaction time of 77 min, catalyst concentration of 0.67 % (w/w), and MTOR of 6:1 for the biodiesel yield of 86.2 %. The physicochemical parameters of the obtained biodiesel were analyzed and were found within the biodiesel standard.

Kusumo et al [188]. evaluated the potential of produced biodiesel from the mixture of *Sterculia foetida* oil (SFO) and rice bran oil (RBO). The oils were blended in varying ratios to undergo the two processes viz. esterification and ultrasound-assisted alkaline transesterification process. The blend of the equivalent proportion of SFO and RBO (50:50 %) was selected due to lower kinematic viscosity, density, and acid value for acid-catalyzed esterification reaction using 1 vol % of H₂SO₄ at MTOR of 60 %. Transesterification was carried out using KOH as a catalyst. The ORCs were estimated by BBD-based RSM which reported an optimum biodiesel yield of 99.93 % in 50.64 min with 0.7 wt % of KOH dosage and 42 % MTOR. They stated that RSM was effective in finding the ORCs and the experimental biodiesel yield was 98.49 %.

9. Fatty acid composition of biodiesel produced from mixed oils

Biodiesel is a mixture of fatty acid alkyl esters as per the description of ASTM. The composition of fatty acids in biodiesel is identical to the raw oil and the nature of fatty acid influences the biodiesel properties [190]. It is revealed that the fuel property varies with the structure of fatty acids such as oxidation stability. The cetane number and heating value increase with the increasing chain length of the fatty acids and decrease with the increase of unsaturation [190]. Biodiesel with long-chain saturated fatty acids has a higher cetane number showing good combustion efficiency and simultaneously possesses high viscosity which creates problems in the atomization of the fuel [191]. A higher concentration of unsaturated fatty acids decreases the viscosity [191]. Thus, properties such as flash point, viscosity, calorific value, density, and cetane index are directly related to the compositions of fatty acids of biodiesel [191,192]. Accordingly, to improve the biodiesel properties, the mixing of various oil feedstocks with suitable fatty acid compositions is one of the encouraging approaches along with cost-effective production at a large scale. A comparative study of fatty acid compositions of

the biodiesel obtained from various mixed oils is presented in Table 5. Adepoju [125] optimized the biodiesel produced from pig fat oil and neem oil (40:60) by a two-step reaction process and reported that the mixed oil contained high amounts of oleic acid (C18:1) and stearic acid (C18:0). In another study, Kumar et al [131]. reported a mixture of karanja and castor oils for the production of biodiesel. It was reported that the hybrid oil contained oleic and ricinoleic acid comprising 44.45% and 35.25%, respectively. Ong et al [134]. reported the mixture of CIO and *Ceiba pentandra* oil (40:60), and Mujtaba et al [126]. reported the mixture of palm and sesame oils (50:50) for biodiesel production. They stated that the oils with higher unsaturated fatty acid content are prone to oxidation. They found that the oil mixture had low saturated fatty acids and resulted in better oxidation stability, and good cold flow properties. In another study, the fuel properties of the canola and lard mixed oil were investigated [127]. They observed that the saturated fatty acids increased with an increase in the amounts of lard oil. The oil blend of waste fish and castor oils [121], and castor and waste chicken oils [136] were studied. It was reported that blending of the oils reduced the ricinoleic acid content due to the reaction that occurred with the hydroxyl group of the ricinoleic acid of the oils. Gupta et al [193]. investigated the ternary oil mixture (palm oil, karanja oil, thumba oil and linseed oil) for biodiesel synthesis and reported that the palmitic and oleic acids contents of palm oil and karanja oil respectively changed after mixing with the thumba oil and linseed oil. Sharma et al [194]. also studied the biodiesel produced from the mixture of karanja, cotton, and jatropha oils via transesterification. They found a decrease in unsaturated fatty acids and an increase in saturated fatty acids. Giwa et al [141]. studied the hybrid oil of palm kernel oil and groundnut oil for biodiesel production. It was reported that the hybrid oil consisted of lauric (24.23%), oleic (35.62 %), and linoleic (15.23 %) acids. Hybrid oil also reported 47.80 % of saturated fatty acid and 52.26 % of unsaturated fatty acid due to the mixture of palm kernel oil (highly saturated oil) and groundnut oil (highly unsaturated oil).

10. Properties of biodiesel produced from mixed oils

The properties such as acid value (AV), calorific value (CV), cetane number (CN), kinematic viscosity (KV), oxidation stability (OS), iodine value (IV), and flash point (FP) are important aspects that determine the performance of the biodiesel produced from different feedstocks. Properties of biodiesel produced from various mixed oils are shown in Table 6. As it can be seen from Table 6 that most of the properties of biodiesels reported from various blended or mixed oils are found as per the conditions set in the standards of EN-14214 and ASTM D6751. AV indicates the weight of KOH (mg) required to neutralize the acidity of 1.0 g of oil. It increases with the presence of water and needs to be reduced to obtain high-quality biodiesel [179]. IV also called iodine number is the measure of the degree of unsaturation of oil or fats or biodiesel. This property influences the ease of oxidation. CV determines the amount of heat that is generated during combustion [195]. FP indicates the lowest temperature at which fuel produces sufficient vapor to produce a flammable mixture in the air. KV determines the measure of fuel flow resistance at a certain temperature. CN indicates the combustion speed of fuel. Long-chain fatty acid and the high saturation level of the fuel attribute to high CN [190,196]. Cloud point (CP) indicates the least temperature at which the fuels begin to form a cloudy appearance on cooling. Pour point (PP) determines the minimum temperature below which the fuel ceases its flow property. OS determines the amount of oil or fat or biodiesel that opposes the degradation on oxidation with air. OS is inversely related to low-temperature properties like CP and PP. It is reported that high saturated fatty acids increase OS, but lower CP and PP, and high unsaturated fatty acid increases CP and PP, but reduces OS [23].

Table 5
Reported fatty acid compositions of the biodiesels obtained from various mixed oils

Feedstock	C10:0	C12:0	C14:0	C16:0	C17:0	C18:0	C20:0	C22:0	C24:0	C16:1	C18:1	C18:2	C18:3	References
Waste fish and Castor seed oils	-	-	0.90	16.19	-	5.63	0.11	-	-	6.73	46.49	11.62	1.73	[121]
Neem and pig fat oils	-	-	-	22.80	-	14.00	-	-	-	1.90	45.20	13.80	2.10	[125]
Palm and sesame oils	-	-	0.48	24.59	-	4.45	0.57	-	-	-	42.48	26.92	0.49	[126]
Canola and lard oils	-	-	0.32	7.13	-	3.36	-	-	-	0.68	60.02	20.13	8.36	[127]
Rubber seed and neem oils	-	-	0.43	18.53	-	2.73	1.69	-	-	0.14	44.43	12.28	1.41	[129]
WCO and <i>Calophyllum inophyllum</i> oil	-	0.18	0.66	30.11	-	7.49	0.61	-	-	0.22	44.78	14.35	0.56	[130]
Castor and karanja oils	-	-	-	13.4	-	2.21	-	-	-	-	44.45	2.85	-	[131]
<i>C. pentandra</i> and <i>N. sativa</i>	<0.1	<0.1	0.1	15.3	0.1	3.1	0.6	0.5	0.3	0.3	23.2	41.0	1.6	[132]
Jatropha oil, karanja oil and cotton seed oil	-	-	0.48	14.8	0.77	-	4.37	20.28	12.66	1.36	-	19.69	-	[133]
Jatropha oil, karanja oil, palm oil and coconut oil	3.51	6.05	4.04	-	13.3	-	9.71	6.06	4.11	-	39.53	7.18	-	[133]
<i>Calophyllum inophyllum</i> and <i>Ceiba-pentandra</i> oils	-	0.1	0.1	16.88	-	15.26	-	-	-	0.2	39.33	19.68	0.3	[134]
WCO and <i>Calophyllum inophyllum</i>	-	0.16	0.66	29.84	-	7.44	0.59	0.00	0.00	0.22	44.81	14.35	0.61	[135]
Castor and Waste chicken oils	-	-	-	12.86	-	4.64	-	-	-	-	25.08	19.09	30.25	[136]
<i>Jatropha curcas</i> and <i>Ceiba pentandra</i> oil	0.1	0.1	0.1	18.6	0.1	4.5	0.5	-	0.1	0.5	36.2	34.3	0.8	[138]
<i>Calophyllum inophyllum</i> and WCO	-	-	-	17.1	-	-	-	-	-	4.2	57.3	15.5	-	[140]
Palm kernel and groundnut oils	1.65	24.23	7.14	8.24	-	2.05	0.46	1.5	0.9	-	35.62	15.23	0.16	[141]
Thumba, karanja, linseed and palm oils	-	-	-	20.4	-	6.7	-	-	-	-	32.2	34.3	14.5	[193]
Jatropha, karanja, cotton seed oils	-	-	0.48	14.8	0.77	-	4.37	20.28	-	1.36	-	19.69	-	[194]

11. Comparison and discussion of biodiesel synthesized from mixed oils

Non-edible oils are gaining worldwide attention as they are cheaper feedstock compared to edible oils, and eliminate the practice of monoculture and thereby retain the soil fertility. Utilization of various mixtures of non-edible oils has been reported by Sharma et al [133], Fadhil et al [137], Dharma et al [138], and Adepoju et al [148] and found to be suitable feedstocks for biodiesel synthesis. Mixing of oils lowered the FFA composition of the raw feedstock. WCO and animal waste are also gaining popularity as they are cheaper than vegetable oils and could reduce the waste generated from slaughter houses, thus reducing environmental impacts and spreading of diseases. Various works on WCO mixed with other oils have been reported in this regard by Milano et al [135], Muciño et al [174], Ramachandran et al [177], Alarcon et al [184], and Hassan et al [189]. They reported biodiesel with good properties as per biodiesel standards. Biodiesel from animal waste is associated with several disadvantages like low oxidative stability, high cold flow property and pour point property. Such problems could be resolved by a mixing approach of feedstocks. In this regard, Fadhil et al [121], mixed castor seed oil with waste fish oil in an equivalent ratio and the resultant biodiesel was found to meet the biodiesel standard. A similar strategy was applied by Issariyakul et al [124], and WCO and canola oil were blended to obtain the feedstock and resulting in an improved biodiesel yield in addition to a better quality of fuel.

Catalyst is a vital part of the alcoholysis of triglycerides. The most reported catalysts in the production of biodiesel from various mixed oils are homogeneous (KOH and NaOH) (Table 4). Though these catalysts produced high yields with good fuel properties, these are economically not feasible due to the issues with the separation and generation of wastewater. The reaction with heterogeneous catalyst is preferred and proceeds in milder conditions in comparison to homogeneous catalyst. However, an acid heterogeneous catalyst, $\text{Al}(\text{HSO}_4)_3$, has been reported by Ramachandran et al [177], for biodiesel synthesis from mixed oil. Though the catalyst was highly active, the reaction needed a high temperature of 220°C which may result in a higher production cost. Similarly, Peng et al [178], synthesized solid catalyst ($\text{SO}_4^{2-}/\text{TiO}_2\text{-SiO}_2$) via impregnation method and performed biodiesel synthesis from mixed oil using the high temperature of 200°C and high pressure. Such catalysts may not be economically feasible for industrial-scale production. Recently, various alkaline biomass-based heterogeneous catalysts have been reported for the reactions of various mixed oils to transform to

biodiesel. These are husk-based catalyst [125], *Enterolobium cyclocarpum* pod husk [129], *Donax deltoids* shells [140], binary mixture of *Lattorina littorea* and *Macra coralline* [173], waste wood ash [175], and K based chicken bone composite [189]. All these catalysts were found to be more cost-effective with high catalytic activity with easy separation process of products and milder reaction conditions (Table 4). Thus, these catalysts have more potential from an industrial point of view. Biodiesel synthesis through the conventional method assumes tremendous time and energy and thus various technologies have been developed to facilitate the rate of reaction. Microwave-assisted transesterification [130] and ultrasound irradiation transesterification [123,126,176] were being applied to biodiesel synthesis from mixed oils because of the advantageous features against the conventional methods. These techniques result in faster conversion in comparison to conventional methods which may benefit efficient and low-cost production.

Various optimization methods like RSM, ANN and ELM have also been employed by various researchers. These methods are very efficient as they reduce the numerous conventional experimental methods to investigate the optimization conditions which are laborious and time-consuming. These methods not only save time but also reduce the material cost of production and improve productivity. One such is RSM which is a statistical tool that can predict the dependent variables (response variables) as a function of the independent variable. Milano et al [130], Dharma et al [138], and Adepoju et al [173] used the RSM tool to maximize biodiesel yield from mixed oils. Falowo et al [147], used Taguchi orthogonal array method to optimize mixed oil biodiesel synthesis using microwave-assisted reaction. Jena et al [144], used the genetic algorithm based on the ANN technique for the transesterification of mixed oil. In another study, Mujtaba et al [126], applied RSM based on the BBD and ELM technique coupled with the cuckoo search algorithm to optimize the process parameters of biodiesel synthesis from mixed oil. They found that the ELM model was more accurate for parameter prediction. Ong et al [134], utilized the ANN model coupled with ACO to optimize the reaction conditions of biodiesel synthesis from mixed oils. Furthermore, they used the RSM model to compare the optimization techniques and stated that the ANN-ACO model was a more simple and reliable tool than RSM.

12. Cost of biodiesel produced from various feedstocks

The global energy demand is predicted to be increased through 2030 causing more scarcity of fossil fuel with the increased price in the market

Table 6
Properties of biodiesels produced from various mixed oils

Biodiesel feedstock	Density (g/cm ³)	Viscosity (40 °C, mm ² /s)	CN	PP (°C)	CP (°C)	FP (°C)	AV (mg KOH/g)	CV (MJ/kg)	SN (mg KOH/g of oil)	IV (g ₁₂ /100gmax)	References
Castor seed oil and waste fish oil	0.8989	3.61	56.97	-2.0	5.0	84	0.06	-	175.24	91.0	[121]
Tung oil, canola oil and palm oil	0.885	4.26								103.52	[123]
Neem and pig fat oils	0.825	2.20	64.62	+3	+5	120	0.42		188.60	47.20	[125]
Palm oil and sesame oil	0.880	4.42	53.37	3.80	7.94	>150	0.37	41.24	-	-	[126]
Thumba oil, karanja oil, linseed oil and palm oil	0.8728	4.69	-	-9	3	198	-	-	-	-	[128]
Rubber seed and neem oils	0.897	5.940	56.53	-6	+15	134	0.410	39.66		68.33	[129]
WCO and <i>Calophyllum inophyllum</i> oil	0.8616	4.72	-	2	2	160.5	0.46	41.35	-	-	[130]
Castor oil and karanja oil	0.9447	7.83	-	12	15	160	0.48	38.63	-	-	[131]
<i>Ceiba pentandra</i> and <i>Nigella sativa</i> oils	0.8669	4.4421	-	-1	0	186.5	0.14	39.945	-	-	[132]
<i>Jatropha</i> oil, karanja oil and cottonseed oil	0.874	3.6	63	-	-	150	4.69	-	168.57	50.88	[133]
<i>Jatropha</i> oil, karanja oil, palm oil and coconut oil	0.877	3.9	60	-	-	150	3.98	-	204.35	55.55	[133]
<i>Calophyllum inophyllum</i> and <i>Ceiba pentandra</i> oil	0.8665	3.72	56	-1.5	-1.0	122.50	0.25	-	-	-	[134]
WCO, <i>Calophyllum inophyllum</i> oil	0.878	5.1262	-	4	3	163.5	0.57	-	-	-	[135]
Castor bean oil and waste chicken oil	0.8898	4.59	-	-4.0	5.0	145	0.12	-	-	98.42	[136]
Radish oil and apricot kernel oil	0.8698	3.31	49.0	-7.0	-	110	0.19	-	-	-	[137]
Radish oil and apricot kernel oil	0.8664	3.41	49.60	-5.0	-	95	0.48	-	-	-	[137]
Radish oil and apricot kernel oil	0.8689	3.23	49.50	-6.0	-	100	0.18	-	-	-	[137]
<i>Jatropha curcas</i> and <i>Ceiba pentandra</i> oil	0.8312	3.950	58	0.5	0.5	196	0.025	40.212	-	-	[138]
<i>Calophyllum inophyllum</i> and palm oil	0.880	4.5	-	-	-	160	0.4	-	-	-	[139]
Palm kernel oil and groundnut oil	0.8657	3.69	>60	-1	3.1	170.2	0.14	-	-	0.457	[141]
Hazelnut oil and sunflower oil	0.8755	4.57	52.67	-18	-13	174	0.29	-	-	83.2	[142]
<i>Jatropha</i> oil and algae oil	-	4.1	-	-	-	115	-	-	-	-	[143]
Mahua oil and <i>simarouba</i> oil	0.860	4.38	-	3.20	-	138	0.479	37.00	-	-	[144]
Mahua oil and <i>simarouba</i> oil (50:50)	0.856	4.77	-	3.60	-	134	0.445	37.02	-	-	[144]
Mahua oil and <i>simarouba</i> oil	0.857	4.56	-	3.50	-	164	0.332	37.01	-	-	[144]
WCO and honne seed	0.888	5.6	62.90				0.54	38.47			[147]
<i>Irvingia gabonensis</i> , <i>Pentaclethra macrophylla</i> , and <i>Elaeis guineensis</i> oil	0.865	1.64	69.75	-	-	-	0.314	-	134.50	76.12	[148]
<i>Carica papaya</i> , <i>Citrus sinensis</i> and <i>Hibiscus sabdariffa</i> seed oils	0.872	1.82	64.38	-12	-2	130	0.36	-	178.24	52.62	[173]
<i>Annona muricata</i> and <i>Calophyllum inophyllum</i> oils	0.860	0.42	74.33	-	-	-	0.42	-	120.20	77.24	[175]
<i>Jatropha curcas</i> oil, castor oil and WCO	0.887	4.08	-	-	2	-	-	36.23	-	-	[176]
Waste sunflower oil palm oil, gingili oil, castor oil, and ground nut oil	0.87	4.1	53	5	6.5	138	-	-	-	-	[177]
Oleic acid and refined cottonseed oil	0.880	3.48	53.4	-6	-	175	-	41.8	-	-	[178]
WCO	0.88	4.89	-	-	3	120	0.43	-	-	-	[181]
Waste fish oil, bitter almond oil, WCO	0.8688	3.26	-	-7	-	176	0.16	-	-	-	[183]
Waste frying oil and palm oil	0.8772	-	56.6	-	-	-	-	39.80	-	-	[184]
Sunflower and soybean oil	-	4.7	62	-9	7	160	0.22	37.5	-	-	[185]
Neem oil and pongamia oil	0.82	4.5	66.26	-2	8	178	0.42	-	-	-	[187]
<i>Sterculia foetida</i> and rice bran oil	0.878	4.89		-6	-5	165	0.364				[188]
EN-14214 standard	0.86-0.90	3.5-5.0	51 (min)	NS	NS	120 (min)	0.5 (max)	NS	NS	1.20 (max)	
ASTM D6751 standard	0.880	1.9-6.0	47 (min)	-15 to 10	-3 to -12	130 (min)	0.8 (max)	NS	NS	NS	

[4]. Researchers are targeting to deal with the declining situation by substituting with renewable energy, especially with biofuels such as bioethanol and biodiesel. The cost of biodiesel will play a significant role to cope with economic viability and acceptability as an alternative fuel

for the future. Cost of feedstocks, fixed cost, and variable cost are the key factors on which the total cost of produced biodiesel generally depends [197]. Approximately 70-95 % of the major production cost of biodiesel is contributed by the cost of oil feedstocks [198,199]. In most countries,

edible vegetable oil is utilized as the feedstock for biodiesel synthesis [20]. Edible vegetable oils are costly due to the huge demand for food. Accordingly, the cost of biodiesel synthesis becomes high and it is a residual problem to be a compatible fuel as an alternative to conventional fossil fuel [200]. Thus, the high cost of feedstock is the major drawback in biodiesel production [201]. However, the cost of biodiesel varies country-wise as well as region-wise due to the varying cost of feedstocks [202]. Tasić et al [203]. suggested the utilization of non-edible low-cost oils or waste oils as feedstocks instead of virgin edible oil to overcome the drawback. In recent times, the production of biodiesel from WCO and non-edible oil sources is emphasized. A comparative list of biodiesel production costs of some edible and non-edible oil feedstocks is summarized in Table 7. Barnwal and Sharma [204] reported the comparison of biodiesel production cost of non-edible pongamia oil with some edible oils. In the report, the huge difference in the biodiesel production cost between high-cost edible oils and low-cost non-edible oil feedstocks is noticed (Table 7). The report also elucidated the dependency of the production cost on the feedstock price. Sesame oil with its high price produces biodiesel at a cost of 1.192 USD/L, while the estimated biodiesel production cost from pongamia oil was 0.232 USD/L [204]. Haas et al [205]. studied a model to estimate biodiesel production cost using soybean oil. They reported a production cost of 0.53 USD/L (2.00 USD/gal) with a feedstock cost of 0.52 USD/kg, which is 88 % of the total estimated production cost. Amigun et al [206]. studied the cost prediction of biodiesel production in Africa following Germany and explored the production cost of biodiesel (0.486 USD/L) from rapeseed oil. Less expensive WCO is one of the preferred feedstocks for economic biodiesel production. In this regard, Mohammadshirazi et al [207]. analyzed the energy and cost of biodiesel production from WCO and reported a higher biodiesel production cost of 1.201 USD/L. In the cost analysis of biodiesel production from pongamia oil, Doddabasa [197] found 0.907 USD/L as the production cost and stated that

the cost of feedstock is the major factor for the cost of biodiesel which is 60 % of the total cost. Patel and Sankhavara [208] stated a similar biodiesel production cost of 0.999 USD/L for karanja oil. Nevase et al [209]. reported the comparative biodiesel production cost of 0.536 USD/L from JCO. Tasić et al [203]. analyzed the cost of stimulated base-catalyzed biodiesel production from sunflower oil and found it to be 0.990 USD/L, and hence, emphasized the use of waste oil or non-edible oil as feedstock. Acevedo et al [210]. reported an identical biodiesel production cost of 0.99 USD/L from palm oil. Utilizing waste chicken fat as low-cost feedstock, Rao and Ramakrishna [201] estimated the cost of biodiesel production and reported it to be 0.392 USD/L. As per the report of Olkiewicz et al [211], biodiesel produced from lipid extracted from municipal wastewater sludge provides a biodiesel production cost of 1232 USD/t. Avinash and Murugesan [212] performed the economic analysis of biodiesel synthesis from WCO and found a biodiesel production cost of 0.752 USD/kg. Similarly, Miranda et al [213]. analyzed the biodiesel production cost from WCO and reported it as 0.1318 USD/L which is comparable with the reported value of Olkiewicz et al [211].. Joshi et al [215]. reported a comparable biodiesel production cost of 0.407 USD/L from WCO, which is well comparable with the production cost reported by Rao and Ramakrishna [201] for waste chicken fat (0.392 USD/L). The several studies showed biodiesel production cost of 0.75 USD/L from rapeseed oil [216], 0.68 USD/L from CIO [214], 0.77 USD/L from castor oil [199] and 0.68 USD/L from palm oil [216]. In all cases, the feedstock price is the major contributor to the production cost. In addition to feedstocks, the production process also contributes a huge to the price of biodiesel. In this regard, Karmee et al [198]. studied the techno-economic evaluation of biodiesel production from WCO by acid, base, and lipase-catalyzed transesterification. They reported the production cost of 750.38 USD/t for acid-catalyzed, 868.60 USD/t for base-catalyzed, and 1047.97 USD/t for lipase-catalyzed transesterification. The high production cost for

Table 7

Comparative summary of biodiesel production cost reported by several researchers from different countries

Feedstock oil	Biodiesel production process	Production Cost of biodiesel	Year of estimation ^a	Country of origin	References
Pongamia oil	Base catalyzed transesterification	0.907 USD/L	2014	India	[197]
WCO	Base catalyzed transesterification	868.60 USD/t	2014	Hong Kong	[198]
WCO	Acid catalyzed transesterification	750.38 USD/t	2014	Hong Kong	[198]
WCO	Lipase catalyzed transesterification	1047.97 USD/t	2014	Hong Kong	[198]
Castor oil	Zn-CaO catalyzed transesterification	0.77 USD/kg	2020	India	[199]
Waste chicken fat	KOH catalyzed transesterification	0.392 USD/L	2015	India	[201]
Sunflower oil	Base catalyzed methanolysis	0.990 USD/kg	2013	Serbia	[203]
Pongamia oil	Base catalyzed Transesterification	0.232 USD/L	2004	India	[204]
Linseed oil	Base catalyzed Transesterification	0.299 USD/L	2004	India	[204]
Coconut oil	Base catalyzed Transesterification	0.411 USD/L	2004	India	[204]
Groundnut oil	Base catalyzed Transesterification	1.065 USD/L	2004	India	[204]
Mustard oil	Base catalyzed Transesterification	0.852 USD/L	2004	India	[204]
Sesame oil	Base catalyzed Transesterification	1.192 USD/L	2004	India	[204]
Safflower oil	Base catalyzed Transesterification	1.109 USD/L	2004	India	[204]
Sunflower oil	Base catalyzed Transesterification	0.888 USD/L	2004	India	[204]
Soya been oil	Base catalyzed Transesterification	0.668 USD/L	2004	India	[204]
Soybean oil	NaOH catalyzed transesterification	0.530 USD/L	2006	USA	[205]
Rapeseed oil	Base catalyzed transesterification	0.486 USD/L	2008	South Africa	[206]
WCO	KOH catalyzed transesterification	1.201 USD/L	2012	Iran	[207]
Karanja oil	Base catalyzed transesterification	0.999 USD/L	2013	India	[208]
Jatropha oil	KOH catalyzed transesterification	0.536 USD/L	2012	India	[209]
Palm oil	Acid catalyzed esterification and base catalyzed transesterification	0.990 USD/L	2013	Colombia	[210]
Lipid	Acid catalyzed esterification/ transesterification	1232 USD/t	2016	Spain	[211]
WCO	NaOH catalyzed transesterification	0.752 USD/kg	2017	India	[212]
WCO	NaOH catalyzed transesterification	0.1318 USD/L	2017	Brazil	[213]
<i>Calophyllum inophyllum</i> oil	Zn-CaO catalyzed transesterification	0.68 USD/kg	2020	India	[214]
Used cooking oil	KOH catalyzed transesterification	0.407 USD/L	2018	India	[215]
Rapeseed oil	Transesterification	0.75 USD/L	2020	Europe	[216]
Palm oil	Transesterification	0.68 USD/L	2020	Indonesia	[216]
Microalgae oil	Alkali-catalyzed transesterification	0.275 USD/L	2020	Portugal	[217]
Sunflower oil	Enzymatic transesterification	0.71 USD/L	2017	Croatia	[218]

^a Year of manuscript received for publication or year of analysis.

lipase-catalyzed transesterification is due to the high cost of the lipase catalyst. Similarly, Budzaki et al [218]. reported the high production cost of biodiesel (0.71 USD/L) from sunflower oil using enzyme-catalyzed transesterification and stated that the high production cost is due to the high cost of the enzyme. The little higher production cost of palm oil biodiesel (0.99 USD/L) was reported by Acevedo et al [210]. that involved both esterification and transesterification processes using acid and base catalysts, respectively. The utilization of two catalysts in two steps increases the production cost. Conclusively, the choice of low-cost feedstock and inexpensive production process are the determining factors in the economically viable production of biodiesel. Used/waste oil and non-edible oil feedstocks, blended feedstocks, low-cost catalyst as well as the efficient process for the production of biodiesel will bring hope to bio-energy research in the near future for its sustainable usage.

13. Prospects and economic feasibility of mixed oils for biodiesel synthesis

Energy is a crucial factor for the economic development of society. Liquid fuel is playing a key role as 81 % of the global energy production is satisfied from fossil resources [219,220]. As an alternative to fossil fuel, biofuel is the renewable source of energy for sustainable economic development in the coming future [219]. Transport and allied sectors are the major consumers of energy and are dominated by fossil fuels [221]. To get rid of the adverse effects on the environment due to increased utilization of fossil fuels and energy crisis, biodiesel amongst the biofuels is emerging as an appropriate alternative. The sustainability and acceptability of biodiesel as a substitute to petrodiesel are dependent on feedstock availability worldwide and biodiesel cost. The feedstock is the major factor that is driving the biodiesel cost and contributing 70-95 % of overall production cost [198,199]. The utilization of edible oil in biodiesel production is not considered economical due to the food vs fuel debate and increasing demand for food due to population growth [200]. However, the application of non-edible low-cost oils, as well as waste oils, may reduce the cost of biodiesel [203]. In addition to that, mixing available non-edible oils, and non-edible oils with waste oils as feedstocks for the production of biodiesel is encouraging and getting more attention in recent times. For refinery-scale production of biodiesel, locally available oil feedstocks and easily importable low-cost non-edible oils will also supplement in reducing the production cost. The quality of produced biodiesel is also a dominating factor for acceptability as fuel. Literature reveals various constraints in producing good quality biodiesel from single oil feedstock and accordingly, the utilization of mixed oil feedstock is suggested to get better quality fuel [23]. Mixing of oil feedstock having poor quality of fuel properties with good fuel properties of oil improves the overall properties for good quality biodiesel output. Conclusively, to compete with the present and future demand of fuel and for the sustainable economic development of society, cost-effective and quality biodiesel production is a prime issue for biorefinery. Mixing of oil feedstock may suitably overcome the contexts of feedstock availability with cost-effective raw materials for large-scale production of biodiesel. Mixing of feedstock will certainly help in optimizing the fuel properties to make it compatible with fuel standards for utilization in the engine with efficient performance and longevity.

14. Life cycle assessment of the production of biodiesel

Though biodiesel is a renewable and potential green alternative to fossil fuel, its traditional production process is being under question in terms of environmental viewpoint [222,223]. The solvents, chemicals, energy used and generation of waste and wastewater in the production of biodiesel are deterrents in terms of impact on the environment [223]. Today's scientific community is in high concern about the overall impact on the environment from the global biodiesel production

processes starting from the harvesting, extraction of oil, processing, synthesis, usage, recycling, and disposal [224]. Life cycle assessment (LCA) is a method applied to evaluate the overall impact of a product, process, and human activity on the environment in all stages of its life cycle from material acquisition, through production and utilization, to waste management [224,225]. It can play an important role in public-private environmental management [226]. In biodiesel production, the significance on the environment from the cultivation stage to the usage in diesel engines as well as disposal of byproducts are the point of anxiety and LCA can be a tool to evaluate these parameters. The idea of LCA was developed in the late 1960s and its wide applications in the different fields were reported in the late 1980s [227]. In 1992, the Centre of Environmental Science–Leiden University in collaboration with the Netherlands Organization for Applied Scientific Research, and Fuel and Raw Materials Bureau developed a guide on environmental LCA [226]. LCA analysis reveals the environmental aspect of a product or process alteration or selection, as well as the presentation of an accurate depiction of potential environmental back-and-forth [225]. LCA is useful in addressing cross-media problems and avoiding the transfer of a problem from one medium to the other or from one place to the other [225]. According to ISO 14040 series, a typical LCA consists of four stages viz. (a) goal and scope definition, (b) life cycle inventory analysis, (c) life cycle impact assessment, and (d) interpretation of result [228]. The system boundary and its functional units are determined and formulated in goal and scope definition. Data associated with the input material and energy streams as well as output environmental emissions are assembled in life cycle inventory analysis. The data are translated to potential environmental impact in LCA followed by conclusion for decision-making purpose drawn in the interpretation of result [229].

Several researchers examined the environmental impacts of the process of biodiesel production. Dutch and German scientists from 1991 to 1994 carried out a comparative study of biodiesel to examine the environmental impact [230]. Spirinckx and Ceuterick in 1994 [230] studied a systematic LCA on the use of biodiesel to assess the overall environmental impact. In 2009, Lardon et al [231]. reported the LCA of biodiesel production from microalgae and assessed the energy balance as well as potential environmental impact starting from biomass production to biodiesel combustion. Well-to-wheel, well-to-gate, cradle-to-grave, and cradle-to-gate are some reported system boundary considerations under goal and scope definition in the LCA of biodiesel [222, 232-235]. Accordingly, the functional unit of biodiesel in the LCA was found to be 1000 kg of biodiesel, and 1 MJ of biodiesel [233 236]. In the life cycle inventory analysis, foreground and background data are reported to be required in which material and energy utilized in the process are included in the foreground, and the data obtained from the production process and processing of materials and energy are considered for background data [222,237,238]. Abiotic depletion, abiotic depletion (fossil fuels), global warming potential (GWP), ozone layer depletion, human toxicity, freshwater aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, eutrophication, and potential acidification are some of the reported environmental impact categories in LCA of biodiesel [235,238,239]. A comparative analysis of environmental impact categories in the LCA of biodiesel synthesis is listed in Table 8. It has been reported that the transesterification stage cause 68% of the total environmental impact in the biodiesel production system [239]. Table 8 reveals a large variation in the GWP in the different reported biodiesel production processes. Regarding GWP, Ripa et al [240]. reported the least potential of 0.32 kg CO₂ eq for WCO catalyzed by KOH, whereas Harding et al [242]. reported a high potential of 4051 kg CO₂ eq for rapeseed oil catalyzed by NaOH. The abiotic depletion potential is found to have a minimal impact among the impact categories in biodiesel production (Table 8). The highest human toxicity potential of 157.55 kg 1,4-DB eq was reported by Al-Muhtaseb et al [236]. for CaO/CeO₂ catalyst in waste loquat oil biodiesel synthesis. However, 145 and 143 kg 1,4-DB eq for the rapeseed oil catalyzed by NaOH and enzyme (*Candida antarctica*) respectively were reported by

Table 8
Comparative life cycle impact assessment of biodiesel synthesis from various feedstocks

Impact category	Unit	Feedstock materials used in biodiesel synthesis via esterification/transesterification										
		KOH [240]	KOH [238]	KOH [240]	NaOH [241]	NaOH [242]	Eggshell derived CaO [243]	Bifunctional CaO/CeO ₂ [236]	Magnetic Fe ₂ O ₃ nanoparticle [244]	Enzyme [242]	Acid and base [239]	
Biodiesel feedstock	-	WCO	WCO	Rapeseed oil	Palm oil	Rapeseed oil	WCO	Waste loquat oil	Waste date oil	Rapeseed oil	WCO	
Abiotic depletion	kg Sb eq	4.66 × 10 ⁻³	-	1.11 × 10 ⁻²	1.32	16	6.93 × 10 ⁻²	0.00	0.00	15.4	5.51	
Abiotic depletion (fossil fuels)	MJ	-	-	-	-	-	-	15657.48	812.09	-	-	
Global warming potential (GWP)	kg CO ₂ eq	0.32	-	2.62	28	4150	8.23	541.32	48.18	4050	299.60	
Ozone layer depletion	kg CFC-11 eq	-	9.50 × 10 ⁻¹⁰	-	-	8.27 × 10 ⁻⁴	8.09 × 10 ⁻⁷	0.00	0.00	7.77 × 10 ⁻⁴	5.80 × 10 ⁻⁵	
Human toxicity	kg 1,4-DB eq	9.66 × 10 ⁻²	-	1.12	-	145	1.10	157.55	20.96	134	106.97	
Freshwater aquatic ecotoxicity	kg 1,4-DB eq	-	3.07 × 10 ⁻¹	-	-	14.1	1.62 × 10 ⁻¹	44.98	26.69	12.4	19.18	
Marine aquatic ecotoxicity	kg 1,4-DB eq	-	-	-	-	2.77 × 10 ³	6.10 × 10 ²	1.74 × 10 ⁵	7.87 × 10 ⁴	2.52 × 10 ³	1.39 × 10 ⁵	
Terrestrial ecotoxicity	kg 1,4-DB eq	-	3.52 × 10 ⁻²	-	-	2.71	1.00 × 10 ⁻²	0.04	0.06	1.72	0.52	
Photochemical oxidation	kg C ₂ H ₄ eq	7.58 × 10 ⁻⁵	-	1.18 × 10 ⁻³	0.146	1.45	7.75 × 10 ⁻⁴	0.164	0.01	1.43	0.08	
Acidification	kg SO ₂ eq	1.19 × 10 ⁻³	4.49 × 10 ⁻⁵	1.70 × 10 ⁻²	1.417	30.2	1.18 × 10 ⁻²	2.604	0.26	29.3	1.39	
Eutrophication	kg PO ₄ ²⁻ eq	1.74 × 10 ⁻⁴	2.02 × 10 ⁻⁶	5.47 × 10 ⁻³	0.673	37.5	1.48 × 10 ⁻³	0.084	0.17	37.5	0.10	

Harding et al [242]. It is revealed from the LCA that the use of non-recyclable homogeneous base catalysts (KOH, NaOH) in the biodiesel production process generates huge wastewater causing an impact on the environment. Recyclability up to four times of magnetic Fe₂O₃ catalyst in the transesterification of waste date oil was reported by Al-Mawali et al [244]. Chung et al [243]. reported five times recyclability of chicken eggshell derived CaO catalyst for waste cooking oil. Good recyclability of bifunctional CaO/CeO₂ catalyst for transesterification of waste loquat oil was reported [236]. Catalyst plays a vital role in biodiesel synthesis, particularly in energy consumption and greenhouse gas emission, and accordingly has an impact on the environment [245]. The availability of feedstock in the production site or minimum transportation will reduce the energy consumption as well as GWP by releasing minimum CO₂ to the environment. In this regard, the utilization of mixed oil as per the availability of biodiesel feedstock will reduce the impact on the environment. The LCA of biodiesel production from mixed oil will reveal an idea about the mixing of quality feedstock for biodiesel production with minimal impact on the environment.

15. Second generation biodiesel feedstocks

The researchers examined a wide variety of biodiesel feedstocks including animal fats, algal, and microbial lipids, and WCO [115]. Edible oils are considered to be the first generation biodiesel feedstock. It causes the shortage of food supply, and it requires a large cultivation area, fertilizers, and water supply which elevate the production cost of feedstocks and biodiesel as well [246,247]. To meet the primary challenge regarding food scarcity by utilization of edible oils, emphasis on non-edible oil feedstocks is given and is getting increasing attention globally. Non-edible oils are the second generation feedstocks for biodiesel [22,248]. Some second generation (non-edible) biodiesel feedstocks along with the oil contents (wt %) and oil yields (kg oil/ha) are listed in Table 9. A flowchart showing the production of biodiesel from

the second generation feedstock [247] is depicted in Fig. 2. The utilization of such non-edible oils has reported substantial benefits for biodiesel. Food limitation and inequality can be eradicated through the use of non-edible crops, and farmland requirements can be reduced as non-edible crops are tolerant and adaptable to different environmental conditions for growing. These can be cultivated in low-fertility land, less humidity, hilly terrains, uncultivated, and wastelands. Restoration of degraded lands and repair of wastelands are huge opportunities for the cultivation of second generation feedstocks [272]. Such feedstocks do not compete with crops, do not affect food prices, and can resist disease and pests. These are also having the potential to produce useful by-products, for example, seed cakes which are used for biogas production [22,115,247,272]. Additionally, the growing of more non-edible crop plants and trees can establish the reduction of carbon dioxide [273]. Lignocellulosic biomass is also getting increasing attention in recent times as a potential candidate for biodiesel synthesis [274]. Besides second generation feedstock, the sources of third generation biodiesel feedstocks are poultry fat, chicken fat, animal tallow, fish, algae, and WCO or waste frying oil [247, 275-279]. These feedstocks are facing problems that interfere with the food chain, and require high production costs even though third generation biodiesel feedstocks can be produced on small farms [115,280]. However, Leong et al [281]. recently studied to enhance microalgal biomass production by employing a microalgal-photobioreactor and reported biodiesel production. Kadir et al [282]. studied a technique for harvesting microalgae via ozonation pre-treatment and reported biodiesel synthesis. Hoang et al [283]. suggested the utilization of 20:80 rice bran oil biodiesel and petrodiesel blend due to acceptable characteristics of combustion and performance of the engine. However, more research and development needs to be carried out using advanced technology to intensify the process using different feedstocks, and ethanol may be used in place of methanol [284]. Abomohra et al [285]. critically studied fat, oil and grease (FOG) based biodiesel synthesis and stated that FOG is a

Table 9
Some second generation (non-edible) biodiesel feedstocks

Non-edible oil sources	Seed oil content (wt %)	Oil yield (kg oil/ha)	References
Sea mango (<i>Cerbera odollam</i>)	54	1900–2500	[249,250, 251]
Milkweed (<i>Asclepias</i>)	20–25	-	[252] [253]
Neem (<i>Azadirachta indica</i>)	30	2670	[254]
<i>Croton tiglium</i> Linn	45.0	-	[255]
Rubber seed (<i>Hevea brasiliensis</i>)	40	40–50	[252] [256]
Fabaceae (<i>Crotalaria retusa</i>)	15	-	[257]
Polanga (<i>Calophyllum inophyllum</i>)	65	4680	[258, 259]
<i>Garcinia indica</i>	44.0	-	[255]
Niger seed (<i>Guizotia abyssinica</i>)	50–60	-	[260]
Cuphea (<i>Cuphea</i> ssp.)	30–36	-	[252]
<i>Jatropha curcas</i>	20–60	1900–2500	[261] [262]
Mahua (<i>Madhuca indica</i>)	30–50	-	[263]
<i>Melia azadirach</i> Linn	45	-	[255]
<i>Raphanus sativus</i>	40–45	-	[258]
<i>Michelia champaca</i> Linn	32.2	-	[255]
Karanja (<i>Milletia pinnata</i>)	30–50	900–9000	[251]
Jajoba (<i>Simmondsia chinensis</i>)	45–50	1413	[264] [250]
Tobacco (<i>Nicotiana tabacum</i>)	35–49	1170	[251]
koroch seed (<i>Pongamia glabra</i>)	33.6	225–2250	[258]
Castor (<i>Ricinus communis</i>)	45–50	1188	[247,265]
Linseed (<i>Linum usitatissimum</i>)	35–45	-	[266]
Pilu (<i>Salvadora oleoides</i>)	45	-	[266]
Chinese tallow seed (<i>Stillingia</i>)	44.15	-	[247]
Kusum (<i>Schleichera trijuga</i>)	10–65	-	[263]
<i>Samadera indica</i>	35	-	[258]
Soapnut (<i>Sapindus mukorossi</i>)	51	-	[267]
Poon (<i>Sterculia foetida</i>)	50–55	-	[266]
Field pennycress (<i>Thlaspi arvense</i> L.)	20–36	-	[258]
Tomato seed	32.1–36.9	1170	[268] [251]
Tung (<i>Vernicia fordii</i>)	30–40	450–600	[251]
Paradise tree (<i>Simarouba glauca</i>)	-	900–1200	[259]
Cotton (<i>Gossypium</i> sp.)	17–25	649	[250,251]
Yellow oleander (<i>Thevetia peruviana</i>)	8.41	1575	[250] [259]
Mexican prickly poppy (<i>Argemone mexicana</i>)	22–36	-	[250]
Persian lilac (<i>Melia azedarach</i>)	10	-	[259]
Moringa (<i>Moringa oleifera</i>)	33–41	-	[250]
Candlenut (<i>Aleurites moluccanus</i>)	60–65	16000	[251]
Bottle tree (<i>Brachychiton rupestris</i>)	50–60	250–300	[251]
<i>Datura stramonium</i>	10.3–23.2	-	[250,263]
<i>Euphorbia lathyris</i>	48	-	[250,263]
<i>Sapium sebiferum</i>	12–29	-	[250,263]
<i>Pistacia chinensis</i>	30	-	[250,263]
Siberian apricot (<i>Prunus sibirica</i>)	44.73–57.83	-	[265]
<i>Mesua ferrea</i>	70–75	-	[265]
Chinese spice (<i>Zanthoxylum bungeanum</i>)	27–31	-	[265]
Radish	33.55	-	[269]
Wild mustard	34.11	-	[270]
<i>Xanthium spinosum</i>	35.30	-	[271]

strong competitor in terms of economical point of view due to its lower cost compared to other feedstocks. Thus, FOG may also supplement the future biofuel industry. Recently, a new carbon-negative source has been introduced as the fourth generation biodiesel feedstock which includes photobiological solar biodiesel, synthetic cell, and electrobiofuels [247]. But this could not surpass the benefits of second generation feedstock as the production of biodiesel from fourth generation does not work for all algae species because of lacking gene and biological information [247,248]. Thus, second generation feedstocks have a high potential for producing biodiesel. These feedstocks have significant roles to substitute fossil fuels and to fulfill the more energy demand. At the same time, the third and fourth generation biodiesel feedstocks may boost the biorefinery sector if the research at the advanced level goes in the right direction [248].

16. The latest trends in biodiesel production

In recent times, biodiesel synthesis using Machine learning (ML) technology is getting more attention among global researchers to improve production efficiency and enhance economic viability [286]. ML algorithms are mainly important and can be applied to determine the complex correlations from the bulky data sets [287]. Various parameters such as reactor type, feedstock type, catalyst type, and operation mode, and process intensification method should be taken into consideration while ML technology is applied in biodiesel production processes. Different powerful ML algorithms applied for predicting different parameters are linear regression (LR), Support vector machine (SVM), Artificial neural network (ANN), Multilayer perceptron neural network (MLPNN), Bayesian regularized neural network (BRNN), Adaptive network based fuzzy inference system (ANFIS), Least square support vector machine (LSSVM), Simulated annealing (SA), Particle swarm optimization (PSO), Kernel-based extreme learning machine (KELM), Principal component analysis (PCA), Genetic algorithms (GA), Extreme learning machine (ELM), and Cuckoo search (CS) [286,288]. The ML technology applications in the process of biodiesel production are categorized into ultrasound-assisted, microwave-assisted, mechanically-assisted, supercritical alcohol, and enzyme-catalyzed transesterification processes [286].

16.1. Ultrasound-assisted transesterification (USAT) process

Ultrasound can be classified into low-frequency (20–100 kHz) and high-frequency (1,000–10,000 kHz) sounds. The introduction of ultrasonic irradiation in the transesterification process leads to cavitation of bubbles close to the phase boundary of alcohol-oil [289]. The consequent cyclic formation, growth, and asymmetric breakdown of the generated bubbles increase the pressure (above 1000 atm) and temperature (above 5000 K) of the reaction medium. In addition, the phase boundary of alcohol-oil is disrupted due to the generation of micro-turbulence, leading to severe mixing between the reactants [290, 291]. Many parameters such as sound power, irradiation frequency, type and quantity of alcohol, type and amount of catalyst, and geometry of the reactor influenced the performances of the USAT process. Tan et al [290]. could successfully estimate the purity and yield of biodiesel from JCO under ultrasonic irradiation by applying the MLPNN model. Maran and Priya [292] found that the MLPNN model was superior to the RSM model for estimating the biodiesel yield on USAT of non-edible oil. Thangarasu et al [293]. applied MLPNN and RSM models for predicting the biodiesel yield from *Aegle marmelos* oil. Results showed that the MLPNN model can predict more accurately than the RSM model. Naderloo et al [294]. and Mostafaei et al [295]. tried to estimate the energy ratio, productivity, and biodiesel yield from WCO under ultrasonication using the LR, RSM and ANFIS models. For all the parameters considered, the ANFIS model could predict more accurately in comparison to RSM and LR models. Mujtaba et al [126]. optimized the process parameters of biodiesel synthesis from palm-sesame mixed oil

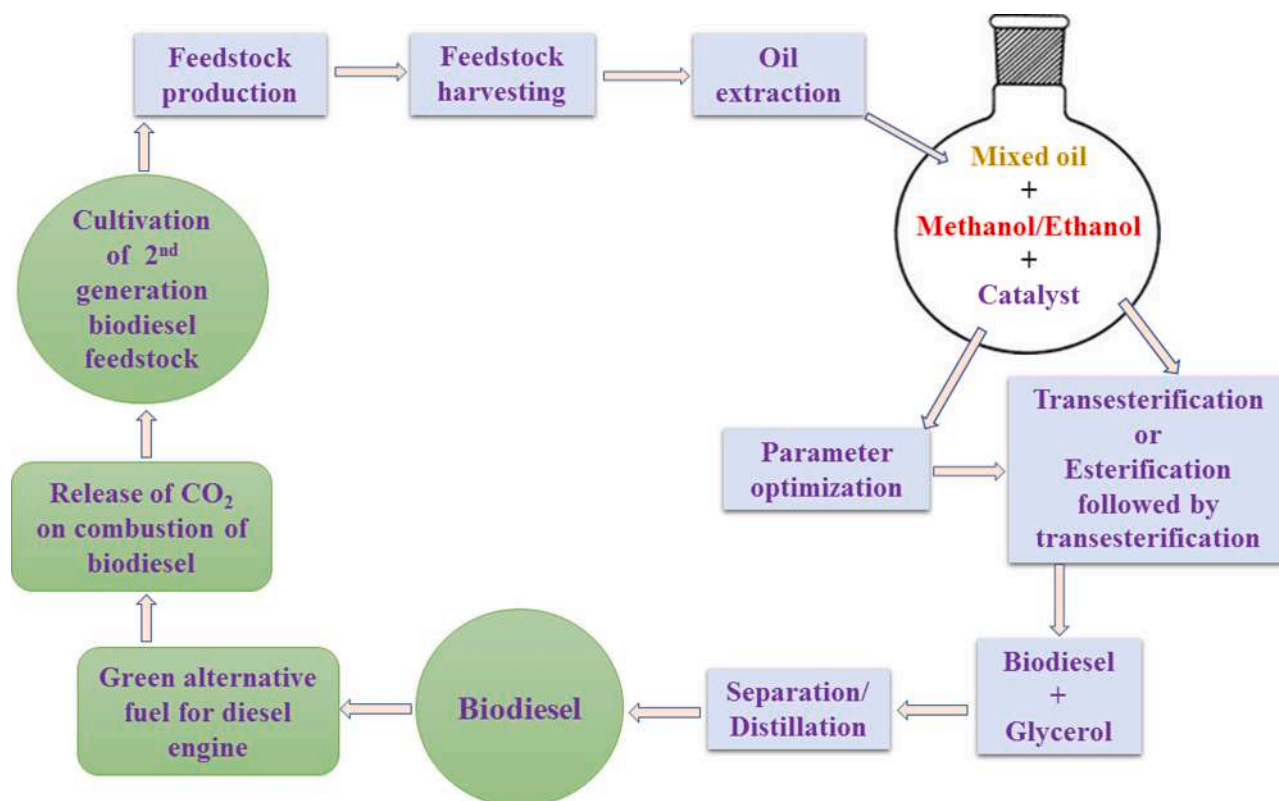


Fig. 2. Production of biodiesel from the second generation feedstock [247].

using the RSM tool based on the BBD and ELM technique coupled with the cuckoo search algorithm. They reported that the ELM model predicted the synthesis of biodiesel more accurately.

16.2. Microwave-assisted transesterification (MWAT) process

A microwave-assisted method is a modern technique that has more advantages than other techniques due to quick heating and overall better efficacy [296]. Microwave consists of wavelength and frequency respectively in the range of 0.01-1 m and 0.3-300 GHz. On irradiation with microwave energy, the polar molecule absorbs its energy and releases it in the form of thermal energy. Moreover, a microwave influences the ion migration/dipole rotations [297]. Due to the presence of both polar and ionic compounds in the reacting agents, alcohol, oils, and catalysts, effective and rapid heating is achieved on irradiation with the microwave. This concentrated heating method is an efficient method for improving the transesterification process [298]. The MWAT process depends on several parameters, including reactors used, wavelength and frequency of the electromagnetic field, feedstocks, type and quantity of alcohol, and type and amount of catalyst. Ma et al [299]. applied MLPNN and RSM models to predict the oil esterification under the MWAT process. The results indicated that the MLPNN model showed better efficiency in comparison to the RSM model. Selvaraj et al [300]. found that the MLPNN model was more precise than the constructed RSM model for predicting the biodiesel yields from WCO under the MWAT process. Silitonga et al [301]. applied both the ELM approach and CS algorithm to model the process yield and optimize the reaction parameters during MWAT of *Ceiba pentandra* oil. From the results obtained, it was confirmed that the combined model was efficient for optimizing the process. Wali et al [302]. demonstrated the ability of the classical fuzzy logic, ANFIS, and adaptive controllers to monitor and control a pilot-scale microwave reactor that was applied for producing biodiesel from WCO in real-time analysis. Falowo et al [129]. reported biodiesel from neem oil and rubber oil mixture via MWAT process using

calcined biomass catalyst. A maximum biodiesel yield of 98.77 % was investigated using CCRD coupled with RSM. Milano et al [130]. utilized the MWAT process for biodiesel synthesis from the mixture of CIO and WCO (30:70). They optimized the reaction using RSM and reported 97.40% of yield. They further investigated with the conventional transesterification method and found that the biodiesel yield from the same oil blend was very low (89.15%) compared to that obtained from the MWAT process. Thus, the MWAT process was found to be more effective than the conventional method.

16.3. Mechanically-assisted transesterification process

In this process, the reactants such as oils, catalysts, and alcohol are heated up to the desired temperature, followed by blending to a mechanical stirring tool in a batch reactor. Different variables such as reaction temperature, residual time, mixing intensity, type and quantity of catalyst, alcohol/oil ratio and the reactor can influence the biodiesel yield. Both MLPNN and RSM approaches were applied in modeling the mechanically-stirred reaction process of various edible and non-edible oils with different base and acid catalysts by several researchers [303–307]. All the authors reported that the MLPNN model could effectively predict the biodiesel yield compared to the RSM model. Kavitha and Murugavelh [308] found that the quadratic RSM model was more accurate than the MLPNN model in modeling the biodiesel yield from *Sterculia foetida* oil with KOH catalyst under mechanical agitation. Etim et al [309]. and Dharma et al [310]. combined the MLPNN approach with the GA paradigm and were able to optimize the process of several non-edible oils under mechanical agitation. Hariram et al [311]. coupled the BRNN model with the GA approach to find the ORCs of CIO reaction. It was reported that the developed BRNN-GA model could adequately estimate the ORCs. Nasef et al [312]. combined the MLPNN approach with the SA algorithm to model the process yield and ORCs of triacetin transesterification under mechanical stirring. Results indicated that the developed MLPNN-SA approach could successfully predict and

optimize the considered variables. Kusumo et al [313]. compared the KELM approach with the MLPNN in generalizing the process yield of the mechanically-assisted process of *Ceiba pentandra* oil. Sohpal et al [314]. reported that the ANFIS model could predict the biodiesel yield of JCO during the mechanically-assisted butylation process. Ighose et al [315]. coupled the ANFIS approach with the GA paradigm to model and optimize the methylation process of yellow oleander oil under mechanical agitation. Ishola et al [316]. coupled the RSM, MLPNN, and ANFIS approaches with the GA paradigm to model the process yield and optimize the reaction conditions of *Hibiscus sabdariffa* oil under mechanical agitation. The ANFIS-GA combination was more efficient for modeling and optimizing the results in comparison to other approaches. Kumar et al [317]. and Sajjadi et al [318]. applied RSM and ANFIS models in estimating the biodiesel yield of base-catalyzed methylation process of non-edible feedstocks under mechanical agitation. They developed that the ANFIS model was found to be more accurate than the RSM model.

16.4. Supercritical alcohol transesterification process

In a supercritical medium, transesterification of low-quality oils with high FFA contents can be carried out. In this process, the oils and alcohol mixture behaves as a single uniform phase. This technique has various merits such as the requirement of no separation of catalyst, no soap formation, shorter reaction time, no sensitivity towards FFAs and water present in the feedstocks. However, this process requires high pressure and temperature and high ATOR [319]. Farobie et al [320]. found that the MLPNN model was efficient for predicting the FAME/FAEE contents of canola oil under supercritical methanol/ethanol conditions. By applying the MLPNN model, Farobie and Hasanah [321] could predict the canola biodiesel yield under supercritical conditions. Srivastava et al [322]. developed an RSM model to predict the biodiesel contents of microalgae and mahua oils. Selvan et al [323]. found that the developed ANN-GA model could predict the biodiesel yield from *Aegle marmelos* oil and could find out the ORCs.

16.5. Enzyme-catalyzed transesterification process

This process has lower energy consumption than the other methods since the reaction occurs at mild temperature and pressure conditions and does not require feedstock pretreatment. The enzyme lipases extracted from biological systems are used for biodiesel production. However, the main drawbacks of this process are the high cost of the enzyme and the long reaction time, preventing its commercialization so far [51,324,325]. Ying et al [326]. applied the MLPNN model for predicting the biodiesel yield of saponified and acid-treated rapeseed soap in the presence of *Candida rugosa* lipase. Results showed that the MLPNN model could estimate the biodiesel yield with an acceptable accuracy limit. Karimi et al [327]. tried to estimate the process yield and energy efficiency during the production of WCO biodiesel in the presence of lipase immobilized onto magnetic nanoparticles using MLPNN and RSM models. It was found that the MLPNN model was better in predicting the output variables in comparison to the RSM model. Zarei et al [328]. reported that the developed RSM model was more accurate than the MLPNN model used in jatropha biodiesel production in the presence of immobilized lipase-catalyst. Amini et al [329]. coupled the MLPNN model with GA and optimized the basil oil methylation process catalyzed by Novozym 435. This model was suitable for predicting the process yield and ORCs.

17. Conclusions and future directions

Biodiesel is an emerging alternative, renewable, and environmentally friendly biofuel for transport and allied sectors. In the production of biodiesel, various methods could be applied viz. transesterification, direct use and dilution, micro-emulsification, and pyrolysis. Transesterification is the most widely used method since it is proved to be

simple, low cost, and more advantageous than other methods because the produced fuel exhibits higher cetane number, lower emissions, and higher combustion efficiency. It has been found that various researchers reported single oil feedstocks for biodiesel production. Single oil feedstock faces issues like non-availability and high production cost. To overcome the shortages of single oil feedstocks and to improve the properties and performance characteristics, many researchers are recently working to produce biodiesel from various blends of edible and non-edible oils including WCO and different fats. It is seen that the blending of two or more oils resulted in biodiesel having fuel properties as per the limits set up by ASTM D6751 and EN 14214 standards. It was found that low-grade oil can be mixed suitably with oils having good fuel properties for the synthesis of high-quality biodiesel. The oils with higher unsaturated fatty acid content are prone to oxidation. Mixing of oil can maintain this required structural composition for good quality biodiesel. This could produce biodiesel with high oxidative stability and cold flow property. The density and viscosity were also found to be reduced after mixing of oils indicating the longevity of the fuel engine and its performance.

Catalyst is a vital part of the alcoholysis of triglycerides. The most-reported catalysts in the production of biodiesel from various mixed oils are homogeneous (KOH and NaOH). Though these catalysts produced high yields with good fuel properties, these are economically not feasible due to the issues with the separation and generation of wastewater. The reaction with heterogeneous catalyst is preferred and proceeds in milder conditions in comparison to homogeneous catalyst. It was found in this study that heterogeneous catalysts such as $\text{Al}(\text{HSO}_4)_3$ and $(\text{SO}_4^{2-}/\text{TiO}_2\text{-SiO}_2)$ could produce biodiesel from mixed oils but needed very high reaction temperatures. Such catalysts may not be economically feasible for industrial-scale production. Several biomass-based alkaline heterogeneous catalysts were reported for the reactions of mixed oils to transform to biodiesel. These biomass-based solid catalysts could produce mixed oil-based biodiesel successfully and were found to be more cost-effective with high catalytic activity, an easy separation process of products, and milder reaction conditions. Thus, these catalysts have more potential from an industrial point of view.

Biodiesel synthesis through the conventional method assumes tremendous time and energy and thus various technologies have been developed to facilitate the rate of reaction. Microwave-assisted and ultrasound irradiation transesterifications were being applied to biodiesel synthesis from mixed oils because of the advantageous features against the conventional methods. These techniques result in faster conversion in comparison to conventional methods which may benefit efficient and low-cost production. Various optimization ML techniques like RSM, ANN, and ELM were also employed for mixed oil-based biodiesel synthesis. These methods are very efficient as they reduce the numerous conventional experimental methods to investigate the optimization conditions which are laborious and time-consuming. These methods not only save time but also reduce the material cost of production and improve productivity. One such commonly employed technique is RSM which is a statistical tool that can predict the dependent variables (response variables) as a function of the independent variable. It was found that these ML techniques were more accurate for the prediction of ORCs.

Biodiesel from animal waste is associated with several disadvantages like low oxidative stability, high cold flow property, and pour point property. Such problems could be resolved by a mixing approach of feedstocks. Thus, the mixing of oil feedstocks (hybrid oils) for biodiesel synthesis will bring revolution in the biofuel sector and will encourage the usage of low-grade oils. Mixing of oils may overcome the issues related to the availability of biodiesel feedstock and production cost. This also promotes the possibility of large-scale biodiesel production with improved fuel quality and may satisfy its large-scale industrial and transport demand. Still there is an issue with the production cost at commercial level and stability of mixed oil-based biodiesel. Therefore, there is a need for more rigorous research and development for biodiesel

production from mixed oils with more improvement in terms of fuel quality from mixing of any type of oil feedstocks and also to make it more cost-effective, and this is a challenge for the biorefinery sector. A suitable reactor needs to be found out along with the competitive solid catalyst to make the process more efficient and to reduce the overall production cost. Application of ML technique will certainly help biodiesel production process from mixed oil. Searching for low-cost pre-treatment and the addition of low-cost ingredients for overall improvement of low-grade biodiesel feedstock may also be needed.

Declaration of Competing Interest

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

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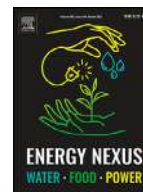
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Biodiesel as renewable biofuel produced via enzyme-based catalyzed transesterification

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ABSTRACT

Biodiesel is a renewable alternative biofuel to conventional fossil fuel. Biodiesel can be produced through esterification and transesterification reactions mainly catalyzed by acid, alkali, and enzyme catalysts. Among all of these catalysts, enzyme catalysts are more advantageous than chemical catalysts (alkali and acid catalysts) due to their high selectivity, mild reaction conditions, lower energy consumption, and yielding of good quality of products with no side reactions. However, because of the high costs of enzymes, there is a limit on the use of enzymatic operation on an industrial scale. The cost of enzymes can be reduced by improving the lifespan of catalysts. Over the last few decades, significant developments in enzyme-based biodiesel synthesis have been attained both on the laboratory and industrial scale, and production costs are also reduced. This review gives an overview of immobilized lipase-catalyzed and lipase-inorganic hybrid nanoflowers catalyzed biodiesel production, including the economic viability of enzyme catalysts and idea about different reactors which is used for enzymatic transesterification reaction.

1. Introduction

Substantial research has been carried out over the past two decades on the development of renewable and sustainable energy such as solar energy [1], tidal energy [2], biofuels (bioethanol, biodiesel) [3], and wind energy [4]. Biodiesel has many advantages compared to other fuels due to its clean combustion, potent substitute for fossil fuels, and applicability as fuel for transportation in heavy-duty vehicles [5,6]. It is understood that the fatty acid methyl esters (FAME) also known as biodiesel is the most feasible alternative energy source to fossil fuel due to their environmental benefits and better performance associated with their usage [7–9]. Combustion of biodiesel releases a relatively small amount of CO₂ which is absorbed back by the plant through the photosynthesis process and protects the natural environment and maintains the ecological balance compared to conventional fossil fuel [10]. The emission of SO₂ in the combustion of biodiesel is lower due to the presence of low sulfur content that effectively reduces acid rain, which represents a serious threat to the environment and humans in the forms of acidification of soil, surface and groundwater, forest, and vegetation damage, and increased corrosion of buildings and historical monuments. Moreover, due to the complete combustion of biodiesel, there is the discharge of a low amount of CO, hydrocarbon, and particulate matter. Biodiesel is nontoxic, biodegradable and renewable diesel fuel [11,12].

Biodiesel (FAME) can be chemically produced from edible oils, non-edible oils, waste cooking oil (WCO), animal-derived fats, and microalgal lipids via esterification or transesterification process reacting with short-chain alcohols such as methanol or ethanol [13–15]. Methanol is found as the most commonly utilized alcohol in biodiesel synthesis due to its low price, high activity and green chemistry metrics [16–20]. It has been found that in total biodiesel production, biodiesel obtained from edible oil feedstocks contributes more than 95%. In biodiesel synthesis, elevated reaction temperature is especially needed for low-grade vegetable oils with high free fatty acid contents or high moisture contents [21–24]. Biodiesel can be produced from a variety of feedstocks (Fig. 1) and the properties are quite similar to conventional diesel [25]. Studies showed that biodiesel fuel obtained from vegetable oil can be used properly on diesel engines [26–29]. The major contributor of edible oils as a feedstock in the synthesis of biodiesel are rapeseed oil (84%) and sunflower oil (13%) followed by palm oil (1%) and the remaining are from groundnut, soybean, coconut, peanut, corn, and canola (2%) [30]. *Jatropha curcas* (Jatropha), *Milletia pinnata* (karanja), *Ricinus communis* (castor), *Madhuca longifolia* (mahua), *Nicotiana tabacum* (tobacco) rubber, *Calophyllum inophyllum* (polanga) and *Thevetia peruviana* (yellow oleander) are the non-edible oil feedstocks for biodiesel synthesis [13,31–34]. Lard, tallow and poultry fat are the animal-derived feedstocks for the synthesis of biodiesel [35]. Recently, mixed (hybrid) oil has been reported as the potential feedstock for biodiesel synthesis [25]. Recycled oil and grease, generally from restaurants and food processing plants, are the waste oil feedstocks for biodiesel production that

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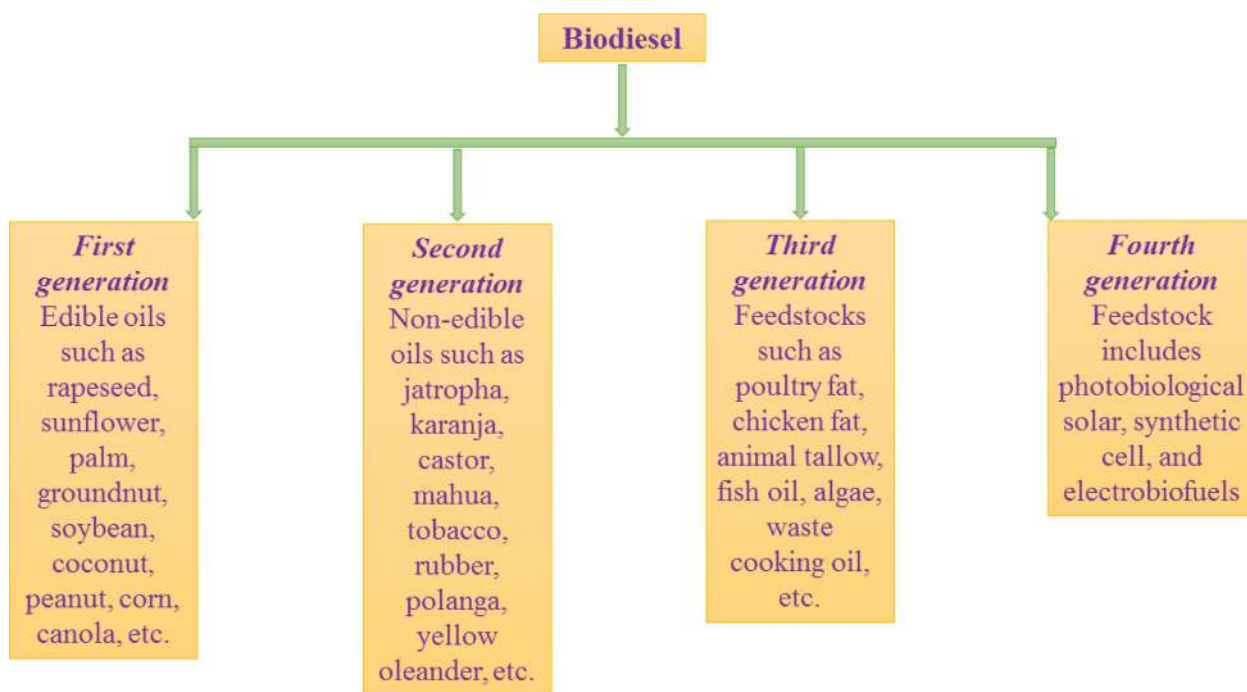


Fig. 1. Different biodiesel feedstocks.

minimizes environmental issues by solving its disposal problems [36]. Recently, microalgae have appeared as the most favorable feedstocks for biodiesel production. Since the rate of microalgal growth and lipid yield is high as compared to plant oil, therefore, microalgal-based biodiesel is considered to have the prospective to meet the high global demand for transportation fuel. The present objection to the step-up of microalgal biodiesel to industrial-scale includes expanding economically-viable microalgal cultivation, biomass harvesting and lipid extraction techniques [37–39].

In transesterification reaction, there are three common kinds of catalysts that are employed *viz.* enzyme catalysts (lipase catalysts), acid catalysts and alkali catalysts. Each catalyst shows merits and demerits in the whole reaction process. The chemical catalysts have several disadvantages like difficulty in glycerol recovery, contamination of product, issues with acidic and alkaline catalyst removal, free fatty acid and water interferences, saponification and formation of soap [40,41]. These issues can be overcome easily if enzyme catalysts are used that require low reaction temperature, low methanol to oil ratio (MTOR) and also enzyme catalysts are environmentally benign. Enzyme immobilization causes eased recovery of products and also permits the reuse of expensive enzymes for different cycles without losing their activity. The enzymatic biodiesel synthesis processes have mild reaction conditions. Generally, enzyme immobilization has been used to achieve reusable enzymes with lower manufacturing costs. Though an enzymatic transesterification of oil is similar to conventional transesterification, an exception is that the reactions are catalyzed by different types of biological catalysts (enzymes) preferably than chemical catalysts. However, one common demerit of the enzyme-based biocatalyst process is the high price of the biocatalyst compared to the conventional alkaline and acid catalysts. Most of the methanolysis reactions (Scheme 1) are catalyzed by lipase enzymes which can be obtained from microorganisms *i.e.* bacteria and fungi. The mechanism of enzyme-based catalyzed biodiesel synthesis [42] is represented in Fig. 2. In the mechanism, the substrate (oil) interacts with the enzyme forming the enzyme-substrate complex. Then the acylated enzyme is formed releasing the diglyceride. The acylated enzyme interacts with methanol leading to the formation of the acylated enzyme alcohol complex. This complex then rearranges to produce biodiesel and the enzyme is regenerated.

Similarly, the enzyme again interacts with diglyceride and then with monoglyceride to form biodiesel molecules. The most commonly used lipase enzymes are *Candida antarctica*, *Mucor miehei*, *Pseudomonas cepacia* and *Rhizopus oryzae* [43–46]. In recent times, several developments in the applications of heterogeneous-based catalysts for biodiesel synthesis are reported. For example, enzymatic metal organic frameworks (MOFs) catalysts [47], ionic liquid-based MOFs [48], lipase-inorganic hybrid nanoflowers [49,50], enzyme-based porous polymeric catalysts [51], heterogeneous nanocatalysts [52], bifunctional heterogeneous catalysts [53], Fe₃O₄-based magnetic catalyst [54], agrowaste-based catalysts [55–60].

2. Enzyme catalyzed biodiesel synthesis from various oil feedstocks

The summaries of performances of various enzyme catalysts in the synthesis of biodiesel from different oil feedstocks are presented in Table 1. Winayanuwattikun et al. [61] investigated 44 plant species available in Thailand and found 27 plants that possess more than 25% of oil. Oils of four species such as palm, physic nut, papaya and rambutan could be highly converted to biodiesel and economically these would be considered as the potential feedstocks for biodiesel production. Among the different plant species investigated, 15 species were found to be the most appropriate as biodiesel feedstock. Amini et al. [62] studied biodiesel production from sweet basil (*Ocimum basilicum*) seed oil (22 wt.%) by lipase-catalyzed transesterification at the optimum reaction conditions (ORCs). These conditions were developed using ANN (Artificial neural network) technique, and 94.58% FAME yield was reported. The immobilized lipase catalyst was found to be reusable till seven cycles of reaction. This study revealed that the biodiesel antioxidant stability did not meet the specification but could be improved by adding antioxidants. Therefore, it was mentioned that *O. basilicum* seed oil showed remarkable potential as a novel source of biodiesel. Su et al. [63] investigated soapstock oil in the production of biodiesel. The soapstock oil contained high free fatty acids (FFAs) and it cannot be effectively transesterified to biodiesel. Hence, a complicated two-stage process *viz.* esterification reaction followed by transesterification was adopted for the conversion to biodiesel. In the present work, one-pot

Scheme 1. Transesterification (methanolysis) of triglyceride to biodiesel.

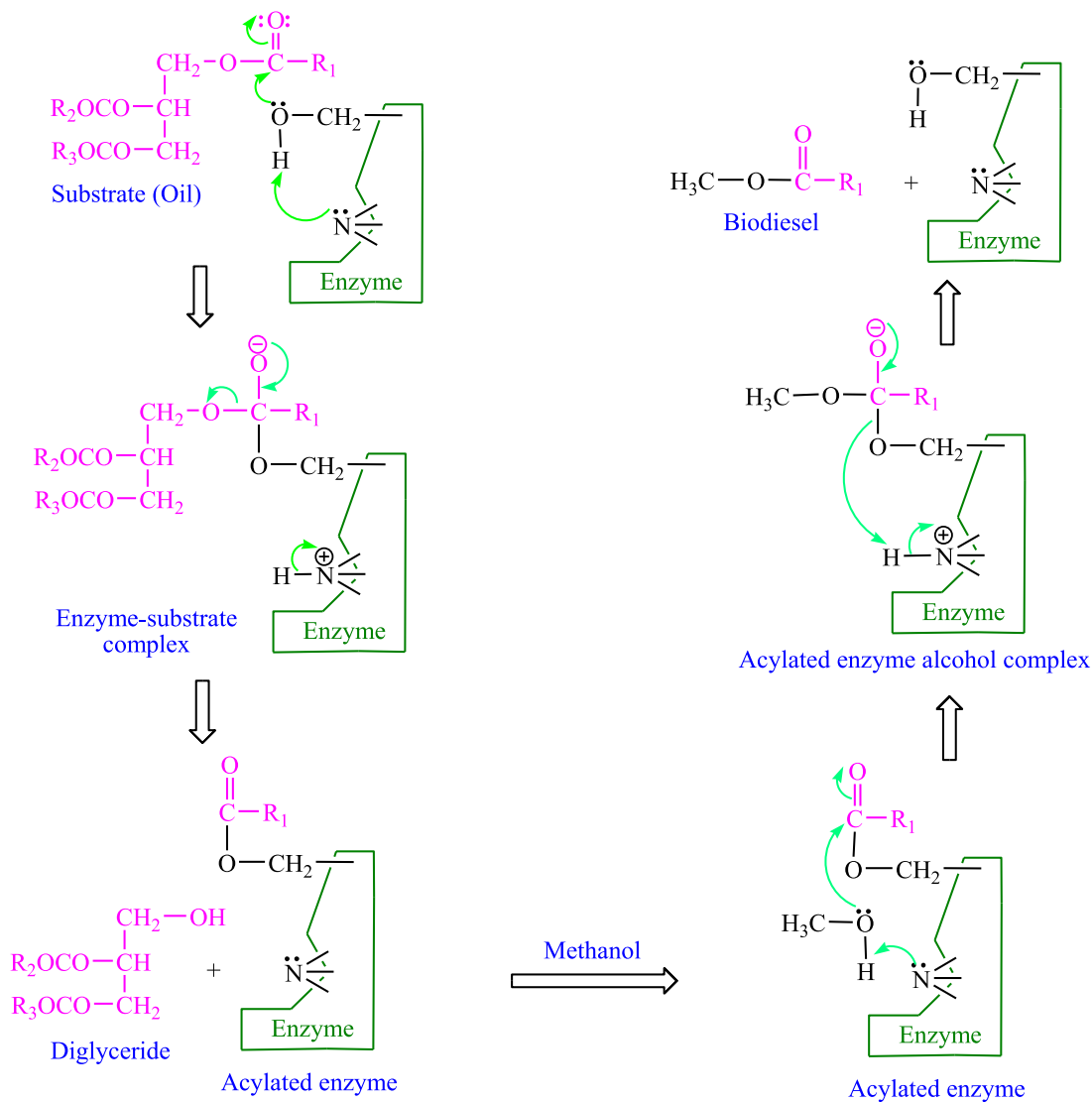
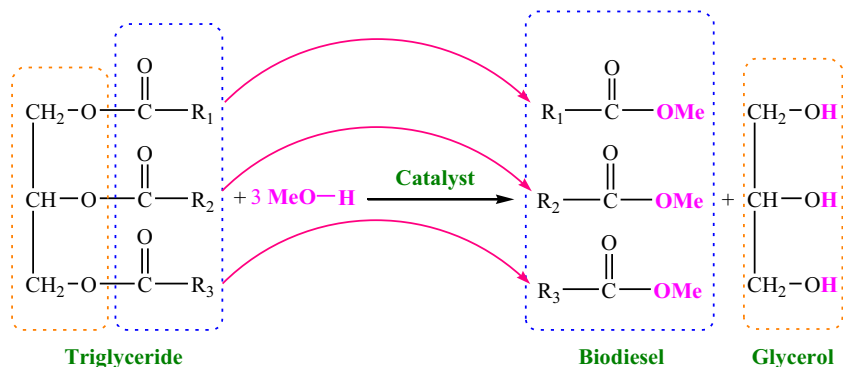


Fig. 2. The mechanism of enzyme-based catalyzed biodiesel synthesis.

esterification and transesterification, the simple one-stage lipase-catalyzed methanolysis of oil were developed. The lipase-catalyzed transesterification of triglyceride in the soapstock oil was severely affected by the water produced through lipase-catalyzed esterification of FFAs. However, this problem was controlled by the addition of tertiary alcohol and increased the FAME yield from 42.8% to 76.4%, which was further uplifted to 95.2% at the optimum reaction conditions (ORCs)

like 5:1 MTOR, 4 wt.% lipase amount, 10-fold 3 Å molecular sieve addition and temperature of 45 °C in 10 h of reaction time. Nguyen et al. [64] investigated the production of biodiesel from insect fat using methyl acetate and the reaction was optimized by response surface methodology (RSM). Oleaginous insects, black soldier fly larvae (BSFL) can assimilate organic waste for fat buildup and provide a feedstock for biodiesel production. In the enzymatic biodiesel production, methyl

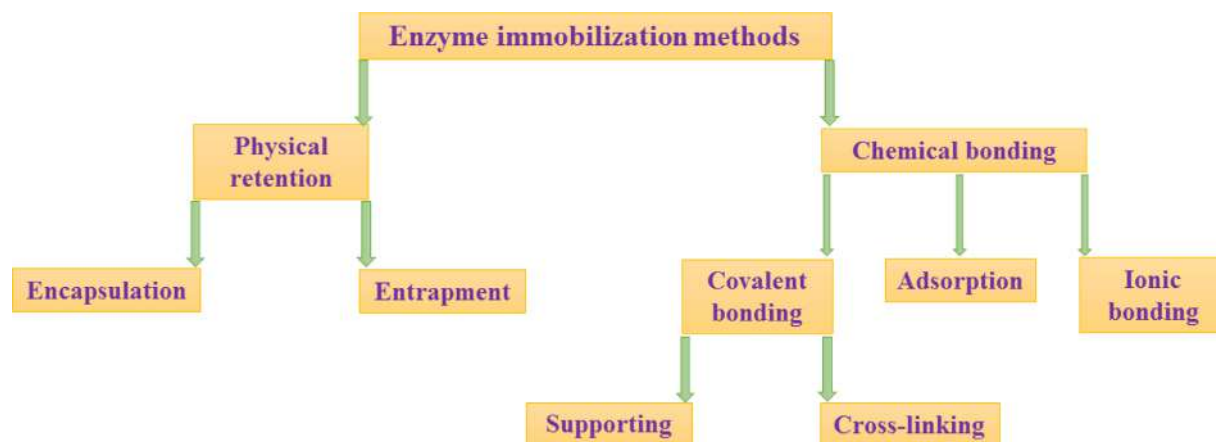


Fig. 3. Methods of immobilization of enzymes.

acetate was utilized first in the study with BSFL (triglyceride source). A high biodiesel yield of 96.97% was achieved under these conditions. Results indicated that Novozym 435 could be reusable up to 20 cycles with insignificant loss in enzyme activity. The BSFL biodiesel contained nine FAME including lauric acid methyl ester (43.22%), palmitic acid methyl ester (19.67%), oleic acid methyl ester (13.03%), and myristic acid methyl ester (8.8%). The properties met the EN 14,214 standard. The authors mentioned that the enzymatic interesterification of BSFL fat by using methyl acetate was a promising and environmentally friendly method for the production of green fuel. Caetano et al. [65] reported the production of biodiesel from oil using enzyme catalyst with ethanol in presence of hexane as co-solvent. Nde et al. [66] investigated the production of biodiesel from mango, neem and shea oils following RSM. In a solvent-free system, these oils were transesterified into biodiesel using immobilized lipzyme enzyme from *Mucor miehei* as the catalyst. The lipzyme enzyme was more tolerant to high temperatures in neem and shea oils reaction in comparison to mango oil. The ORCs of transesterification reactions were different for each oil. The conversion of biodiesel was quantified by ^1H NMR spectroscopy. The immobilized lipase from *Mucor miehei* was reusable up to 10 times. Arumugam et al. [67] studied biodiesel synthesis from fish industry byproduct waste sardine oil as a non-edible renewable source, which contained a relatively FFA value of 32 mg KOH/g of oil. On activated carbon, immobilized *Aspergillus niger* lipase (100 mg) enzyme was used as the catalyst. Studies indicated that the immobilized-lipase catalyst was found reusable for 5 cycles without losing its activity. The study also showed that the 10% blend of waste sardine oil biodiesel with diesel fuel improves the engine performance and minimizes emissions of air pollutants. Jambulingam et al. [68] studied biodiesel synthesis using immobilized lipase functionalized magnetic nanocatalyst from the lipid of oleaginous fungal. Different microbes were isolated from the oil-contaminated soil and tannery effluent and investigated for high lipid content. The fungal strain SF2 indicated the high lipid content among all of the isolates and was identified as *Aspergillus niger*. It was reported that about 44.02% of lipid was produced by the fungi. The lipase enzyme was immobilized onto the prepared Fe_3O_4 magnetic nanoparticles. The magnetic nanoparticle was synthesized by co-precipitation method. TEM experiment showed that the particle size was 20 ± 5 nm. At different parameters, both free and immobilized enzyme esterase activities were analyzed. Results proved that immobilized enzymes displayed better stability, which can be stored for 60 days and reusable up to 5 cycles without any significant loss of activity. By using the lipase immobilized on the magnetic nanoparticle, biodiesel was produced. The immobilized catalyst was found to be reusable for 5 cycles. The biodiesel properties were found within the limit specified by the ASTM standard. Li et al. [69] examined the transesterification of *Pistacia chinensis* oil using methanol

and recombinant biocatalysts *Rhizopus oryzae* lipases immobilized on anion exchange resin and macroporous resin (AI-ROL and MI-ROL). Various types of macroporous and anion exchange resins were used to immobilize recombinant ROL. Biodiesel production from immobilization lipase permitted the use of mild and environmentally friendly reaction conditions. After being used for five consecutive cycles in the reaction using AI-ROL, there was no obvious loss in the yield of biodiesel, but more than 60% yield of biodiesel was maintained even after the MI-ROL was utilized for 4 reactions cycles. Suwanno et al. [70] studied the potential of biodiesel by using residual oil (obtained from palm oil mill effluent) and crude lipase (obtained from oil palm fruit) as an alternative substrate and catalyst. Lipase was extracted from ripened palm fruit and crude lipase was purified by using aqueous two-phase systems. The biodiesel was characterized according to Thai biodiesel and ASTM standards and found that nearly all properties of biodiesel were acceptable. Low FFA (0.07%) and high cloud point (10–13 °C) were observed in the enzymatic synthesis of biodiesel. Rakkan et al. [71] investigated biodiesel synthesis through transesterification of palm oil mill effluent as substrate in presence of hepatopancrease lipase. In the study, using the three-phase system in combination with the aqueous two-phase systems, the crude lipase catalyst was purified. They reported that the properties of biodiesel were similar to conventional diesel and other biodiesel and found within the standards of international specifications. This study indicated the possibility of the use of hepatopancrease lipase as a catalyst. Dhawane et al. [72] investigated biodiesel production from *Mesua ferrea* oil using a developed catalyst via lipase immobilization on microporous activated carbon derived from coconut shells. Immobilization was optimized and found to be 270 min reaction time, 15 °C reaction temperature, 500 mg/L initial concentration of protein, and pH value of 6. They reported an adsorption capacity of 10.04 mg/g. The prepared catalyst showed high stability and was reusable after 5 cycles. During the reaction, insignificant leaching of lipase was attributed to strong binding between lipase and carbonaceous support. Guo et al. [73] developed a method for biodiesel synthesis from frying palm oil which was catalyzed by free *Candida antarctica* lipase A (CALA). The reaction was optimized by RSM and presented that the lipase CALA showed very good methanol resistance. The lipase CALA can catalyze both transesterification and esterification of FFA simultaneously in presence of excess water. Babaki et al. [74] demonstrated the catalytic activity of lipases obtained from *Rhizomucor miehei* (RML), *Thermomyces lanuginosus* (TLL) and *Candida antarctica* (CALB) which were immobilized covalently on epoxy-functionalized silica. The immobilization followed remarkable improvements in thermal stability compared to the free enzyme. These lipases were used in the synthesis of biodiesel from canola oil with methanol. These immobilized catalysts were stable and could be reusable for 16 cycles without significant loss in activities.

Table 1
Catalytic performance of reported enzyme catalysts in biodiesel synthesis.

Biodiesel feedstock (oil)	Catalyst	Reaction conditions					References
		Alcohol to oil ratio (ATOR)	Catalyst (wt.%)	Temp (°C)	Time (h)	Yield (%)	
Physic nut oil	Novozyme 435	3:1	20	55	24	43.8	[61]
Palm oil	Lipozyme RM IM						
	Novozyme 435	3:1	20	55	24	~a	[61]
Papaya oil	Lipozyme RM IM						
	Novozyme 435	3:1	20	55	24	25	[61]
Rambutan oil	Lipozyme RM IM						
	Novozyme 435	3:1	20	55	24	41.3	[61]
Sweet basil (<i>Ocimum basilicum</i>)	Novozym 435	10:1	6	47	68	94.58	[62]
Rapeseed soapstock oil	Novozym 435	5:1	4	45	10	95.2	[63]
<i>Hermetia illucens</i>	Novozym 435	14.64:1	17.58	39.5	12	96.97	[64]
Vegetable oil	Lipozym TL IM	4:1	1.6	35	48	53.6	[65]
Mango oil	Lipozym TL IM	3:1	7.25	36.61	36.42	98.1 ± 1.0	[66]
Neem oil	Lipozym TL IM	3:1	7.19	45.65	25.08	98.5 ± 1.6	[66]
Shea oil	Lipozym TL IM	3:1	4.43	45.65	25.08	99.3 ± 0.4	[66]
Sardine oil	<i>Aspergillus niger</i> lipase	9:1	100 mg	30	10	94.5	[67]
Oleaginous fungal lipid	<i>Aspergillus niger</i> lipase	4:1	–	45	4	84	[68]
<i>Pistacia chinensis</i>	<i>Rhizopus oryzae</i> lipases	5:1	–	37	60	90.3	[69]
Palm oil	Crude Lipase	6:1	–	35	36	92.07±1.04	[70]
Palm oil mill effluent	Hepatopncase lipase	6:1	–	40	12	91.45	[71]
<i>Mesua ferrea</i>	Lipase on activated carbon support	10:1	5	30	10	67.5	[72]
Waste frying palm oil	Lipase A from <i>Candida antarctica</i>	7:1	5.5	30	22	94.6 ± 1.4	[73]
Canola oil	Lipase from <i>Candida antarctica</i>	3:1	13	50	96	68	[74]
Canola oil	Lipase from <i>Rhizomucor miehei</i>	3:1	13	50	96	45	[74]
Waste cooking oil	Lipase from <i>Rhizomucor miehei</i> and lipase B from <i>Candida antarctica</i>	3:1	–	50	10	91.5	[75]
Waste cooking oil	Lipases from <i>Candida rugosa</i> and <i>Rhizomucor miehei</i>	6:1	1	45	24	96.5	[76]
Macauba pulp	Lipases from <i>Rhizomucor miehei</i>	2:1	3	40	8	91	[77]
Waste cooking oil	Lipases from <i>Candida rugosa</i>	3:1	–	35	24	90	[78]
Canola oil	Lipase from <i>Thermomyces lanuginosus</i>	3:1	13	50	96	98	[74]
Blended non-edible oils (waste cooking oil, crude palm oil, rubber seed oil and jatropha oil)	Lipase from <i>Thermomyces lanuginosus</i>	7.64:1	3.55	36	2	90	[79]
Green microalgae lipid	Lipase from <i>Thermomyces lanuginosus</i>		1	30	30	90.24	[80]
Waste cooking oil	Lipase from <i>Candida sp.</i> 99–125	1:1	25	45	30	91.08	[81]
<i>Scenedesmus obliquus</i>	Lipase from <i>Pseudomonas fluorescense</i>	3:1	10	35	12	66.55	[82]
<i>Scenedesmus obliquus</i>	Lipase from <i>Pseudomonas fluorescense</i>	3:1	10	35	12	91.7	[83]
Rubber seed oil	Lipase	10:1	5	30	10	84.05	[84]
<i>Calophyllum inophyllum</i> oil	Lipase	6:1	–	35	6	94	[85]
Palm oil mill effluent	Lipase	6:1	2 g	40	5	44	[86]
Waste cooking oil	Lipase enzyme	3:1	1.5	60	4	88	[87]
<i>Sapim sebiferum</i> oil	<i>Pseudomonas cepacia</i> lipase	4:1	2.7	41	12	96.22	[88]
Hybrid oil	<i>Pseudomonas cepacia</i> lipase	6:1	10	50±1	24	82	[89]
Hybrid oil	<i>Pseudomonas cepacia</i> lipase	5.93:1	9.46	49.7	24.32	85.14	[90]
Jatropha curcas oil	Lipase-PDA-TiO ₂ NPs	6:1	10	37	30	92	[91]
Cyanobacterium <i>Synechococcus elongatus</i>	SBA-15@oleate@lipase	3.4:1	34	37	17	85	[92]
Sunflower oil	QLM@nanoflowers	2:1	80 mg	50	4	94.7	[50]
Soybean oil	Magnetic lipase hybrid nanoflowers	4:1	5	40	24	87.6	[122]
Sunflower oil	PPL@nanoflowers	2:1	100 mg	45	24	96.5	[123]
Sunflower oil	Lipase@Bio-MOFs	8:1	100 mg	50	4	>60	[124]

ATOR–Alcohol to oil ratio; wt–weight; h–hour; Temp–temperature; a–oils obtained from commercial supplier; PDA–Polydopamine; NPs–Nanoparticles.

Babaki et al. [75] also studied the immobilized lipase from *Rhizomucor miehei* (RML) and lipase B from *Candida antarctica* (CALB) onto epoxy-functionalized silica as the covalent binding to the heterogeneous solid carriers makes the enzyme very stable. A multi-enzyme system was developed for biodiesel production from waste cooking oil (WCO). The study indicated that a mixture of 1,3-specific lipase (RML) and non-specific lipase (CALB) was used to increase the yield of biodiesel production. The factors affecting biodiesel yield were studied through central composite rotatable design (CCRD) and RSM. Results of the reusability test indicated that CALB-epoxy was reusable up to 14 cycles and the reusability of RML-epoxy was up to 11 runs which showed the feasibility from an economical point of view. Binhayeeding et al. [76] reported biodiesel synthesis from WCO via enzymatic transesterification. The lipases collected from *Rhizomucor miehei* and *Candida rugosa* were

immobilized on polyhydroxybutyrate to serve as eco-friendly catalysts and this mixture yielded 96.5% of biodiesel. The immobilized lipase catalyst was reusable for more than 6 cycles, and after that, the activity of the lipase decreased. In the present work, eco-friendly biodiesel was produced using WCO, polyhydroxybutyrate as an immobilizing agent and 1% of immobilized lipase. It was reported that immobilized lipases mixtures on polyhydroxybutyrate were highly versatile, and a low catalytic amount was required. Aguietas et al. [77] studied biodiesel production from Macauba (*Acrocomia aculeate*) pulp oil (10.5% acidity) by the enzyme/enzyme hydroesterification process. The hydrolysis of Macauba oil with a vegetable enzyme which was obtained from dormant castor seeds subsequently esterified the FFA with ethanol, and catalyzed by fermented and dry Babassu cake with lipase activity from *Rhizomucor miehei*, producing ethyl esters. Desikan et al. [78] tested an enzy-

matic route for WCO biodiesel synthesis which was performed by using methyl acetate and immobilized lipase as biocatalyst. Immobilization of lipase from *Candida rugosa* was done by the entrapment method. This work approach was found to be a very effective and environmentally friendly novel technique. The important byproduct tri-acetin showed no effect on the fuel property and demonstrated that this process is feasible for large-scale production of biodiesel. Malani et al. [79] investigated ultrasound-assisted biodiesel production using a blended feedstock of non-edible oils in presence of immobilized lipase obtained from *Thermomyces lanuginosus*. Four different non-edible oils such as WCO, crude palm oil, rubber seed oil and jatropha oil were mixed and used in enzymatic transesterification. The volumetric ratio of blended non-edible oils such as WCO, palm oil, rubber oil and jatropha oil was 30%, 30%, 25% and 15%. After sonication, the activation energy of the reaction decreased from 124.4 kJ/mol to 100.4 kJ/mol. In the study, the kinetic analysis of the reaction disclosed that the use of ultrasound and the addition of water to the reaction mixture lowered the activation energy. The addition of water (10% v/v) to the reaction mixture increased the biodiesel yield from 90% to 94%. This process also lowered the activation energy to 78.7 kJ/mol. The catalyst was reusable for 6 cycles. He et al. [80] investigated a novel integrated process for ethanolysis of lipids. The reaction was carried out by three marine *Nannochloropsis* strains viz. *N. oculata*, *Nannochloropsis* sp. and *N. oceanica* to create feasible and clean microalgal biodiesel. The highest biomass (4.38 g/L) and total fatty acids (TFAs) yield (1.55 g/L) was found in *N. oculata* and was selected for the performance of lipid extraction and biodiesel synthesis. Three-phase partitioning (TPP) showed better lipid extraction when the lipid extraction of *N. oculata* cells was handled by four mixed enzymes viz. papain, cellulase, pectinase and hemicellulase. With liquid lipase from *Thermomyces lanuginosus* (TL), the extracted lipids from the ethanol phase of TPP were used directly in the ethanolysis for biodiesel synthesis. Chen et al. [81] utilized WCO for biodiesel production employing immobilized *Candida* lipase. In biodiesel production, the effects of lipase, water, solvent, temperature and flow of the reaction mixture were investigated. Guldhe et al. [82] reported biodiesel synthesis from *Scenedesmus obliquus* lipids with biocatalyst. For the synthesis of biodiesel from lipids, *Candida* sp. and *Pseudomonas fluorescens* free and immobilized lipases with porcine pancreas and wheat gram were investigated. Stepwise methanol addition was applied to improve the conversion of biodiesel up to 90.81%. Studies showed that the immobilized lipase could be used for 4 sets without substantial loss in conversion efficiency. Guldhe et al. [83] also studied biodiesel synthesis from microalgal *S. obliquus* using a tungstated zirconia heterogeneous acid catalyst and compared it with enzyme and homogeneous acid catalysts. The study indicated that the catalyst yielded maximum biodiesel conversion compared to the enzyme and homogeneous acid catalysts in terms of reaction parameters, conversion efficiency, reusability and energy consumption. The heterogeneous acid catalyst was found reusable for up to 3 batches and the enzyme catalyst was reusable for up to 4 batches without any significant loss. Most of the biodiesel properties produced by the heterogeneous catalyst met the conditions set by ASTM and EN standards. Dhawane et al. [84] investigated the activity of the carbonaceous catalyst support for lipase immobilization as a heterogeneous biocatalyst in biodiesel production from rubber oil. The catalyst showed good reusability for 3 cycles, after three cycles yield decrease was about 1%. Arumugam et al. [85] investigated enzymatic transesterification of *Calophyllum inophyllum* oil with a high level of FFA. In the study, a catalyst was synthesized from sugarcane leaf ash and was subsequently functionalized with carboxyl, amino, thiol and phenyl groups for the lipase immobilization. By template-assisted method mesoporous catalyst was prepared and after immobilization, amine-functionalized catalyst retained maximum specific activity of the enzyme. For immobilized lipase, amine-functionalized mesoporous silica catalyst appeared to have maximum percentage immobilization (49%). The immobilized enzyme catalyst was reusable for ten cycles and showed long-term firmness of lipase activity for methanolysis. Matinja et al. [86] reported

biodiesel synthesis from palm oil mill effluent with immobilized *Candida rugosa* lipase which was optimized by RSM. Jayaraman et al. [87] studied the production of WCO biodiesel by enzymatic transesterification in presence of lipase enzyme as the catalyst. Three different test blends such as 20%, 40% and 60% biodiesel blended with diesel were investigated and showed lesser emissions of pollutants than conventional diesel except for emissions of NO_x. Li et al. [88] studied biodiesel synthesis from *Sapium sebiferum* oil using an immobilized lipase catalyst obtained from *Pseudomonas cepacia* G63. At the ORCs, the immobilized lipase was reusable for 20 cycles with good activity. The experiment showed a high biodiesel yield of 96.22% which was in good conformity with the predicted yield of 97.07%. Results of this study suggested that the production of biodiesel from *Sapium sebiferum* oil with the immobilized lipase will be a promising one. Kumar et al. [89] checked the feasibility of biodiesel produced from non-edible hybrid oils (Karanja and Castor) using 2-propanol and bio-supported beads immobilized with lipase from *Pseudomonas cepacia*. Karanja and castor oil were added in equal amounts. The fatty acids present in hybrid oils were palmitic (13.4%), oleic (44.5%), linolenic (2.9%), stearic (2.2%) and ricinoleic acid (35.3%). By taking 2-propanol as an acyl acceptor in absence of solvent under standard conditions, the reusability of immobilized lipase was tested for 12 batches. It was reported that the catalyst was stable up to 9 cycles of reaction, after that the bio-support beads could retain up to ~52% of biodiesel. The present work showed various advantages compared to the conventional method such as no contamination, low-cost for the purification step, less energy consumption and lower environmental concerns. Kumar et al. [90] reported the production of biodiesel from non-edible hybrid oils (Karanja and Castor oils) in a jacketed packed bed bioreactor with immobilized lipase catalyst from *Pseudomonas cepacia*. To study the ORCs, central composite design and RSM were used. After 10 cycles, the bio-support catalyst could retain up to 70% biodiesel yield. The results showed that after 50 days the immobilized lipase produced a high biodiesel yield and even after 60 days, the yield retained 78.58%. Most of the biodiesel properties were found to meet the conditions set by ASTM D6751 and EN 14,214 standards. Zulfiqar et al. [91] developed a nano-biocatalyst (Lipase-PDA-TiO₂ NPs) for enzymatic transesterification of jatropha oil. By the hydrothermal method, TiO₂ NPs were prepared and then modified using polydopamine (PDA) polymer. Using RSM, the transesterification of oil in presence of lipase-PDA-TiO₂ NPs catalyst was optimized. Imanparasat et al. [92] investigated the activity of SBA-15@oleate@lipase as a heterogeneous biocatalyst for the production of cyanobacterium-based biodiesel via transesterification reaction. In the study, the heterogeneous catalyst was prepared by modification of mesoporous silica of SBA-15 using oleic acid and lipase from *Actinomyces sediminis* (SBA-15@oleate@lipase) with maximum activity by a protein load of 32 mg/g. The catalyst was reusable for 5 cycles and the reusability of catalysts indicated the high stability of the heterogeneous system.

3. Lipase-inorganic hybrid nanoflowers (HNFs) catalyzed biodiesel synthesis

Lipase-inorganic hybrid nanoflowers (HNFs) were reported by Ge et al. in 2012 [93]. Lipase-inorganic HNFs are classified as single-enzyme and multi-enzyme HNFs. According to the metal phosphate and application sector, single-enzyme HNFs and multi-enzyme HNFs are also split up [94]. The synthesis process of lipase-inorganic HNFs was environmentally friendly. Besides, lipase-inorganic HNFs owned excessive surface to volume ratio that decreases the mass transfer resistance in substrate, enzyme, and product. Lipase-inorganic HNFs displayed extensive prospective in various implementations including more catalytic activity, greater stability, and preferable reusability in comparison to free enzymes. Lipase-inorganic HNFs are used to fade different types of dyes, for example, laccase-inorganic HNFs can be used for dye decolorization and malachite green degradation [95,96]. Lipase-inorganic HNFs have several applications in biodiesel synthesis, biosensors [97–114],

protein digestion [115,116], enzyme purification [117], biofuel cell [118,119], beer brewing [120] and detergent industry [121]. Li et al. [49] reported the synthesis of lipase-inorganic HNFs using $\text{Ca}_2(\text{PO}_4)_2$ and *Aspergillus oryzae* lipase. They concluded that the metal ion valence state played a salient role in the shape and catalytic activity of lipase-inorganic HNFs. The synthesized lipase-inorganic HNFs established relatively higher catalytic activity by using bivalence inorganic metal ions such as Mn^{2+} , Ca^{2+} , and Zn^{2+} compared to univalent metal ions (Ag^+) or trivalent metal ions (Fe^{3+} , Al^{3+}). Catalytic performance of reported lipase-inorganic HNFs used as catalysts in biodiesel production is also shown in Table 1. Liu et al. [50] developed lipase-inorganic HNFs for biodiesel synthesis from sunflower oil. The lipase-inorganic HNFs were produced by using thermophilic lipase QLM (obtained from *Alcaligenes* sp.) which was effectively immobilized in $\text{Cu}_3(\text{PO}_4)_2$ -based inorganic HNFs by a process called biometric mineralization. To elucidate the effective loading of enzyme molecules, the structure, morphology, and element configuration of enzymes were comprehensively identified. The optimum conditions for temperature and pH of immobilized lipase were determined by observing the p-nitrophenyl caprylate hydrolysis. The immobilized lipase-inorganic HNFs possessed outstanding reusability and durable storage stability. The catalyst was repeatedly used for 8 cycles and the activity of immobilized lipase slightly decreased. Zhong et al. [122] reported lipase-inorganic HNFs mediated biodiesel production from soybean oil via transesterification reaction. The lipase-inorganic HNFs were produced by using the surfactant activated lipase obtained from *Aspergillus oryzae* which was used to produce magnetic HNFs by implanting Fe_3O_4 magnetic nanoparticles. However, using the free lipase, the yield was only 69%. After 6 successive cycles, the biodiesel yield slightly decreased to 76%. Magnetic HNFs and cross-linked-magnetic HNFs activity recovery was 190% and 174%. Without noticeable activity loss, the magnetic HNFs can be simply recycled by a magnet. After being reused for 10 cycles, the activated HNFs and activated magnetic HNFs maintained 26% and 84% of their primary activity, respectively. This indicates the excellent reusability of magnetic HNFs. Jiang et al. [123] reported the utilization of lipase-inorganic HNFs as a catalyst for the synthesis of biodiesel using sunflower oil. The lipase-inorganic HNFs were produced by a simple, profitable, and green process based on biomimetic mineralization using porcine pancreas lipase (PPL) and Cu^{2+} ions. The characterization of nanoflowers showed prosperous encapsulation of lipase in the HNFs. Utilizing p-nitrophenyl caprylate as a framework in the hydrolysis of esters, lipase-inorganic HNFs were noticed to own good catalytic activity. The biodiesel yield remained 72.5% after the 5 cycles of reaction. Li et al. [124] also developed the lipase-inorganic HNFs and applied them as a catalyst in the reaction of sunflower oil to produce biodiesel using methanol. The lipase-inorganic HNFs were produced by using thermophilic lipase QLM obtained from *Alcaligenes* sp. It was effectively immobilized in the bio-based metal-organic framework (Bio-MOFs) by biomimetic mineralization utilizing zinc acetate as a metal ion and adenine as an organic ligand. Thermogravimetric analysis of lipase@Bio-MOFs revealed that the enzyme loading in immobilized lipase was 15.9%. The study displayed good activity and stability of catalyst even in high temperature and alkaline conditions. The ORCs were MTOR of 8:1 and a reaction time of 4 h at 50 °C that yielded >60% of biodiesel. The study showed outstanding recyclability.

4. Properties of produced fame using enzyme-catalyzed reaction

Biodiesel (FAME) must possess properties like diesel fuel so that it can be utilized as a suitable alternative to diesel fuel [125]. The main strategy for the production of hydrocarbon fuels from bountiful resources is to lessen the oxygen content of the feedstock and make C–C bonds between biomass-derived intermediates and accumulate the molecular weight of the hydrocarbons produced [126]. Therefore, the physicochemical properties and qualities of synthesized biodiesel from renewable resources through chemical reactions have perquisite specifications before it is being used and should pursue instruction of in-

ternational standards such as American Standards for Testing Materials (ASTM D6751–3) and European Union Standards for Biodiesel (EN 14,214). Transesterification of oils or fats into biodiesel causes a decrease in the density and viscosity with a little increase in volatility of biodiesel and the produced biodiesel displays nearly close properties to that of diesel fuels [127,128]. The properties of biodiesel are confirmed based on various properties such as density, cetane number, kinematic viscosity, cold filter plugging point, pour point, flash point, iodine number, saponification number, acid value, calorific value and oxidation stability. Oxidation stability and cold filter plugging point are dependent on the types of biodiesel feedstocks. The properties of various biodiesels synthesized by transesterification reactions of several oil feedstocks with enzyme catalysts are presented in Table 2. In general, the properties of biodiesel were found in the range of specified standards. The ignition quality of biodiesel fuel is indicated by its cetane number. This measures the energy contents of biofuel and how much energy is generated at the complete combustion of a particular fuel [61,129]. The higher cetane number of biodiesel indicates better combustion efficiency. When the alkyl chain length and the molecular weight of biodiesel increase, the higher heating value also increases and decreases with increasing the unsaturation of fatty acids [130,131].

5. Reactors used in the enzyme-catalyzed reaction

Most of the enzyme-catalyzed transesterification for biodiesel synthesis is carried out in the shaking flasks in the laboratory. Packed-bed reactor (PBR), stirred tank reactor (STR), fluidized bed reactor (FBR), and bubble column reactor (BCR) are the different types of reactors used for biodiesel production [132].

5.1. Packed-bed reactor (PBR)

PBR is the most favorable reactor and it is used for continual operation. PBR is primarily composed of a column, and in column immobilized lipases are packed [132,133]. PBR has more reacting surface area per unit volume that gives volumetric yield in continual industrial processes in comparison to stirred tank reactor (STR) [134]. Reaction temperature, MTOR, flow rate [135], and solvent content (if used) are considered optimization parameters for the synthesis of biodiesel with PBR. Among all of these parameters, the flow rate is the most important working variable. Because a low flow rate is used to get sufficient retention time for excessive biodiesel yield. But long term operation of PBR still needs improvement as the glycerol generated is settled on the surface of immobilized lipases which decreases the catalytic efficiency and yield of biodiesel [136]. Stepwise addition of methanol, elimination of glycerol and introduction of solvent like *t*-butanol as a reaction medium helps to overcome these limitations [137]. It is found that the PBR can be handled for 3–7 days without a significant decrease in esters yield [138,139]. The disadvantages of PBR are high-pressure drop with little carrier size and obstacles in mass transfer [140]. Because of the higher viscosity in the solvent-free system, pressure drop becomes more remarkable compared to the solvent system. The mass transfer and biodiesel yield are remarkably affected by the flow velocity. The mass transfer influences the yield of biodiesel at a low velocity of the substrate and the biodiesel yield is influenced by the reaction at a high velocity of substrate [141]. In the PBR system, the internal mass transfer exhibited an important impact on the apparent kinetics of biodiesel production [141].

5.2. Stirred tank reactor (STR)

Owing to the simplicity of construction, ease of the operating system, and maintenance, STR is the most frequently used reactor for biotreatment at different scales [132,134]. It is controlled at both batch stirred tank reactor (BSTR, generally used in laboratory) and continuous stirred tank reactor (CSTR, mainly applicable on large scale due to

Table 2
Comparison of the properties of biodiesel produced using various enzyme catalysts.

Biodiesel feedstock	Density at 15 °C (g/cm ³)	Kinematic viscosity at 40 °C (mm ² /s)	Cetane number	Pour point (°C)	Flash point (°C)	Cold filter plugging point (°C)	Acid value (mg KOH/g)	Iodine value (g I ₂ /100 g)	Saponification number (mg KOH/g)	Higher heating value / Calorific value (MJ/kg)	Reference
Physic nut oil	–	3.46	48.91	–	–	–	–	108.40	202	–	[61]
Palm oil	–	3.62	59.11	–	–	–	–	60.07	207	–	[61]
Papaya oil	–	3.69	56.27	–	–	–	–	75.60	202	–	[61]
Rambutan oil	–	3.95	61.17	–	–	–	–	5813	195	–	[61]
Sweet basil (<i>Ocimum basilicum</i>)	0.87	4.26	–	–15	–	–	0.53	–	–	39.72	[62]
Rapeseed soapstock oil	–	–	–	–	–	–	81.9	–	195.6	–	[63]
<i>Hermetia illucens</i>	0.875	5.4	49	–	122	–	<0.8	–	–	–	[64]
Vegetable oil	0.904	8.34	–	–	163	–5	1.70	99	–	38.4	[65]
Mango oil	–	3.25	57.83	13	–	–	0.33±0.008	–	–	–	[66]
Neem oil	–	2.668	64.43	12	–	–	0.18±0.03	–	–	–	[66]
Shea oil	–	5.404	64.75	13	–	–	0.37±0.002	–	–	–	[66]
Sardine	0.891	3.9	56	–	161	16	32	–	–	50	[67]
Oleaginous fungal lipid	0.861	1.427	54	3	136	–	0.293	92	–	–	[68]
<i>Pistacia chinensis</i> seed	0.88	4.15	49	–	102	–	10.6	–	175.7	39.8	[69]
Palm oil	–	5.0 ± 0.42	60±0.1	10–13	–	–	4.82	930.15	201.96±0.21	–	[70]
Palm oil mill effluent	0.89	4.4 ± 0.1	–	2	–	–	0.3 ± 0.1	52	201.96	–	[71]
<i>Mesua ferrea</i>	–	5.6	47	–	130	–	0.8	–	–	–	[72]
Waste frying palm oil	–	–	–	–	–	–	5.51±0.01	–	–	–	[73]
Canola oil	–	–	–	–	–	–	–	–	190.93	–	[74]
Waste cooking oil	–	–	–	–	–	–	–	76	–	196.2	[75]
Waste cooking oil	0.86	3.8	–	–	59.7	–	0.3	–	175	–	[76]
Macauba pulp	0.872	5.01	–	–	151	–	–	–	–	–	[77]
Waste cooking oil	–	–	–	–	–	–	–	–	–	–	[78]
Blended non-edible oils (waste cooking oil, crude palm oil, rubber seed oil and jatropha oil)	0.918	30.153	–	–	–	–	11..68	–	202.32	–	[79]
Green microalgae	–	4.71	57.67	–	–	–	–	70.72	–	–	[80]
Waste cooking oil	0.892	9.12	68	–	195	–2	0.12	–	298.97	–	[81]
<i>Scenedesmus obliquus</i>	0.877	–	51.77	–	–	4.9	0.42	98.68	–	37.67	[82]
<i>Scenedesmus obliquus</i>	–	–	52.67	–	–	–	0.46	93.72	–	38.44	[83]
Rubber seed oil	–	4.9	48	–	149	–	0.13	–	–	43	[84]
<i>Calophyllum inophyllum</i> oil	0.868	3.15	69	–	136	–	0.29	–	–	–	[85]
Palm oil mill effluent	–	4	–	–	181	–	–	–	–	–	[86]
Waste cooking oil	0.875	3.21	–	–3	189	–	0.125	–	–	7489.6	[87]
<i>Sapitum sebiferum</i> oil	0.90	4.81	–	–	72	–10	0.0007	–	–	–	[88]
Hybrid oil	0.8831	7.83	–	12	160	–	0.48	–	–	38.63	[89]
Hybrid oil	0.88	7.85	–	13	160	–	0.47	–	–	39.51	[90]
<i>Jatropha curcas</i> oil	0.873	3.9 ± 0.2	–	–6 ± 1	132±1	–	9.70±0.92	–	157.13±1.03	0.873	[91]
Cyanobacterium <i>Synechococcus elongatus</i>	0.8	2.9	56	–12	–	–16	–	77	201	35.5	[92]

the high productivity) modes. By using STR, high conversion of oil to biodiesel is obtained. STR requires high shearing force, which is a significant drawback of STR. This limitation causes the compensation of the carrier and therefore, it is restricted to the catalyst reusability [136]. The factors affecting the shearing force are stirring speed and the impeller types. Hence, optimization of stirring speed and improvement of the impeller is necessary to reduce the damage of immobilized lipases. In addition, the unreasonably low speed of stirring leads to a low yield of production. This is due to the limitation in mass transfer whereas, unreasonably high speed leads to carrier damage and weakens the enzyme [136].

5.3. Airlift loop reactor (ALR)

ALR works on a solvent system. It has been examined for immobilized lipase-catalyzed transesterification of oils. It has two channels for gas-liquid upflow and downflow [142]. The inject gas leads to the immobilized lipases and reactant blend. A new ALR was designed and patented which does not need external gasses, where at the top the internal gas methanol and t-butanol vapor are recovered by a pump to the bottom and then liquid-solid immobilized lipases can be blended

well [143]. This reactor can prevent the loss of solvents and reactants and can help in the reduction of the production cost. Consumption of energy in the case of ALR is lower than STR. ALR likely does not perform effectively for blending in a solvent-free system. In contrast to STR, ALR consumed less energy and it cannot blemish the carriers. ALR mass transfer needed to be more escalated because the mixing is not so acute. ALR is as likely as not performing efficiently for mixing in a solvent-free system [143].

5.4. Other heterogeneous reactors

Besides PBR, ALR and STR, there are some other heterogeneous reactors reported for transesterification of immobilized lipase-catalyzed reactions [132]. These are fluidized bed reactor (FBR) and bubble column reactor (BCR). Qualification of conventional heterogeneous reactor improves the productiveness and lifespan of immobilized lipases. Qualification of the conventional heterogeneous reactor was done by combination with separation systems such as extraction, adsorption, and membrane to simultaneously get rid of byproducts [144–147]. As a result, the mass transfer resistance is decreased and there is an increase

in the lifespan of immobilized lipase and also increases the difficulty of instruments and operation [144–147].

5.4.1. Fluidized bed reactor (FBR)

The reactants can be well-mixed using this reactor. In FBR, particles must be of almost uniform size. In FBR, the solid catalyst can be stirred vigorously with viscous oil. An extensive study of transesterification reaction using FBR is needed and it needs further improvement for large-scale application [148]. FBR improves heat and mass transfer. However, it causes the leaching of immobilized lipases from the carriers [149]. In contrast to PBR, FBR showed more success in blending the solid catalyst with the viscous oil, prompting a decent contact of immobilized lipase with its substrate [149].

5.4.2. Bubble column reactor (BCR)

Bubble column is a type of reactor, where gas is sprinkled from the base of the column into a liquid phase or liquid-solid interruption [132,150]. In BCR, solid and liquid suspensions are blended well, and the gas phase moves as plug flow. For highly viscous substrates, the bubble column is an excellent reactor. Though the gas included makes the reactor not reasonable for reactions having unstable reactants, it is suitable for shifting the thermodynamic equilibrium of the reaction by eliminating the product immediately. An effective instance of joining the two benefits is the creation of surfactant in BCR from esterification of polyglycerol-3 and lauric acid catalyzed by Novozyme 435, where the produced water is taken out by compressed air ascending through the reactor [151].

6. Immobilization methods of lipases used in biodiesel synthesis

For over a century, Nelson and Griffin first reported the immobilized enzyme [152]. In the last few years, the synthesis of biodiesel in presence of immobilized lipase has fascinated considerable attentiveness. Compared to free lipases, immobilized lipases showed higher superiority like better reusability, quick recovery, greater flexibility for continual performance, and excessive forbearance to reactants and products [140,153]. There are numerous methods for immobilization of lipase and these are adsorption, entrapment, encapsulation, cross-linking, and covalent binding [154]. These methods can be again categorized into reversible and irreversible depending upon the interactions between enzymes and carriers [155]. The classification of the methods of enzyme immobilization [156] is shown in Fig. 3. Several reported immobilization methods of enzymes used in biodiesel synthesis are shown in Table 3. In case of irreversible immobilization, enzymes cannot be separated from supporting materials without damaging either the biological activity or the support of the enzyme. In case of reversible immobilization, the enzyme can be removed easily. For irreversible lipase immobilization, covalent bonding, entrapment, and cross-linking are the most frequently used methods. On the other hand, physical adsorption and several non-covalent bonding methods are used for reversible immobilization. Each lipase immobilization method has its advantages and disadvantages.

Physical adsorption is a well-known method of lipase immobilization. In physical adsorption, various non-covalent interactions are involved such as non-specific, bio-specific, affinity, electrostatic interaction, and hydrophobic interaction [195]. Physical adsorption immobilization is superior to other immobilization methods due to the mild reaction conditions, low-cost carrier material and procedure of immobilization, effortless working principle, easy carrier reconstruction, and no requirement of chemical additives [196]. In adsorption immobilization, mostly used support materials are polypropylene, polyacrylate, polystyrene, etc. [197]. When a derivative of native and hydrophobic lipase is immobilized on polar polymers, it exhibited greater specific activities [198]. The factors affecting the immobilization efficiency are the concentration of enzyme, the ratio of carrier to enzyme, pH, ionic

strength, etc. It has been reported that the ratio of resin to lipase remarkably affects the lipase adsorption kinetics on cross-linked polystyrene resin [199]. When the resin/lipase ratio increases, the equilibrium adsorption magnitude decreases. The ratio can also intensify the adsorption rate constant [199,200]. Similarly, the pH of the buffer is important for immobilization. When pH values are adjacent to the isoelectric point of the enzymes, maximum adsorption is noticed [201,202]. Even though lipase immobilization by physical adsorption is economically excellent because of ease of process and great activity of the enzyme for the synthesis of biodiesel, the steadiness of immobilized lipase is yet to be improved to a greater extent.

The enzymes are bound by salt linkages in ionic bonding immobilization [155]. Usually, the carrier polysaccharides and synthetic polymers are used as ion-exchange residues [153]. Compared with physical adsorption, the inter-linkages between lipase and carrier are much stronger in the case of ionic bonding lipase immobilization. Ionic bonding can be performed under milder reaction conditions than the covalent bonding method. Covalent binding lipase immobilization occurs via a chemical reaction. The chemical reaction takes place between the active amino acid residues and the binding site of the enzymes [197]. Thiol and amine groups of enzymes are used as the covalent binding groups [155]. Polymers, silica gel, chitosan, magnetic particles, etc. are the several types of carriers that have been used for covalent binding. The immobilized lipase accomplished through this method exhibited great stability in the course of the transesterification reaction with nearly no lipase leaching due to the strong binding force between lipase and carrier. Mendes et al. [188] reported that organic medium-based covalent immobilization on epoxy-SiO₂-PVA was found to be the most suitable for lipase immobilization that could provide the highest hydrolytic activity. Zhang et al. [196] outlined that the preparation set up for this method is diligent with the application of some toxic coupling reagents. In the course of the immobilization process, the enzyme might lose its activity and for that reason, the price of this method is high.

Immobilization of lipase by entrapment method represents the capture of enzymes inside a polymeric matrix which permits the substrate and products to transit, but hold onto the enzyme [155,196]. Lipase proteins do not stick to the polymeric network after entrapment immobilization of lipase. Entrapment-mobilized lipases are more reliable than physically adsorbed lipases. This method is easy to carry out compared to covalent bonding. However, a low conversion rate is witnessed in the synthesis of biodiesel via this method. Jegannathan et al. [203] reported a lipase obtained from *Burkholderia cepacia* which can be enclosed into κ-carrageenan with 42.6% efficiency. After 6 cycles of p-nitrophenyl phosphate hydrolysis, the enclosed lipase maintained 72.3% of its original activity. But, after 10 cycles, the yield of biodiesel reduced to 40% when the same lipase was applied for transesterification [189]. Macario et al. [204] reported that physical adsorption immobilized lipase kept only 34% of its original catalytic activity after two reaction cycles, while after ten reaction cycles, the enclosed lipase retained 60% of its catalytic activity. Therefore, they concluded that catalytic stabilities of encapsulation are more than physical adsorption. Other researchers also reported the same results [190,191]. Mass transfer limitation is the main constraint for utilizing this method in the preparation of biodiesel. Another limitation is the byproduct (glycerol) that can escalate the viscosity and attach to the external surface of the carrier.

The lipase immobilization takes place by the development of inter-molecular cross-linkages, which can be attained by the incorporation of bifunctional and multifunctional cross-linking reagents like glutaraldehyde [153]. From fermentation broth, lipase can be precisely immobilized, which is recovered as cross-linked enzymes aggregates (CLEAs). In an aqueous solution, CLEAs remarkably have great stability within a wide diversity of temperature and pH values [192]. Gupta et al. [205] reported that CLEAs can be produced by *Thermomyces lanuginosus* accommodating with glutaraldehyde. After 10 cycles, the aggregates exhibited extra activity greater than 90%. Similar observations were reported by Kim et al. [193]. They compared the stability of cross-linked

Table 3
Reported immobilization methods of enzymes used in biodiesel synthesis.

Lipase sources	Carrier used	Immobilization methods	References
<i>Candida antarctica</i>	Epoxy-functionalized silica	Covalent bonding	[74]
<i>Thermomyces lanuginosus</i>	Epoxy-functionalized silica	Covalent bonding	[74]
<i>Rhizomucor miehei</i>	Epoxy-functionalized silica	Covalent bonding	[74]
<i>Candida rugosa</i> and <i>Rhizomucor miehei</i>	Polyhydroxybutyrate	Adsorption	[76]
<i>Candida rugosa</i>	Methyl acetate	Entrapment	[78]
<i>Thermomyces lanuginosus</i>	Immobead 150	–	[79]
<i>Candida lipase</i>	Textile cloth	–	[81]
<i>Candidarugosa</i>	PVA-alginate-sulfate beads	–	[86]
<i>Pseudomonas cepacia</i>	Polystyrene	Physical adsorption	[88]
<i>Aspergillus oryzae</i>	Ca ₃ (PO ₄) ₂	–	[49]
<i>Alcaligenes</i> sp.	Cu ₃ (PO ₄) ₂	Biomimetic mineralization	[50]
<i>Aspergillus oryzae</i>	Fe ₃ O ₄ magnetic nanoparticles	Coprecipitation and covalent cross-linking	[122]
Porcine pancreas	CuSO ₄ and phosphate buffer saline	Biomimetic mineralization	[123]
<i>Alcaligenes</i> sp.	Zinc acetate and adenine	Biomimetic mineralization	[124]
<i>Candida rugosa</i>	Magnetic particles	Covalent bonding	[144]
<i>Pseudomonas cepacia</i>	Magnetic nanoparticles	Adsorption	[157]
<i>Rhizopus oryzae</i> and <i>Candida rugosa</i>	Silica gel	Co-immobilization	[158]
<i>Candida antarctica</i> B and <i>Rhizomucor. miehei</i>	Epoxy functionalized silica gel	Co-immobilization	[159]
<i>Rhizopus oryzae</i> and <i>Candida rugosa</i>	Silica gel	Covalent bonding	[160]
<i>Thermomyces lanuginosus</i> and <i>Pseudomonas fluorescens</i>	Toyoppearl AF-amino-650 M resin	Multipoint covalent	[161]
<i>Thermomyces lanuginosus</i>	Aldehyde resin	Covalent bonding	[161]
<i>Pseudomonas cepacia</i>	Polydopamine-coated magnetitenanoparticle	Covalent bonding	[162]
<i>Candida antarctica</i> B and <i>Pseudomonas cepacia</i>	Amino functionalised SBA-15	Covalent bonding	[163]
<i>Candida</i> sp. 99-125	Textile membrane	–	[164]
Steapsin	Waste derived activated carbon	Adsorption	[165]
<i>Thermomyces lanuginosus</i>	Zeolites	Physical adsorption	[166]
<i>Pseudomonas</i> sp.	Accurel EP-100	Physical adsorption	[167]
<i>Pseudomonas cepacia</i>	Carbon cloth	Physical adsorption	[168]
<i>Candida antarctica</i>	Activated carbon	Physical adsorption	[168]
<i>Yarrowia lipolytica</i>	Celite	Physical adsorption	[169]
<i>Pseudomonas cepacia</i>	Ceramics	Physical adsorption	[170]
<i>Candida rugosa</i>	Chitosan	Covalent bonding	[171]
<i>Rhizomucor miehei</i>	Hydrophilic resins	Physical adsorption	[172]
<i>Thermomyces lanuginosus</i>	–	Covalent bonding	[173]
<i>Candida rugosa</i>	MCM-41 materials	Physical adsorption	[174]
<i>Thermomyces lanuginosus</i>	Olive pomace	Covalent bonding	[175]
<i>Saccharomyces cerevisiae</i>	Mg-Al hydroxalicates	Physical adsorption	[176]
Steapsin lipase	Polyacrylic bead	Covalent bonding	[177]
<i>Burkholderia cepacia</i>	Nb ₂ O ₅ and SiO ₂ -PVA	Covalent bonding	[178]
<i>Pseudomonas fluorescens</i>	Organosilicate	Physical adsorption	[179]
<i>Pseudomonas fluorescens</i>	Polymethacrylate	Physical adsorption	[180]
<i>Pseudomonas fluorescens</i>	Silica	Physical adsorption	[180]
Lipolases (<i>Aspergillus oryzae</i>)	PVA/chitosan film	Entrapment	[181]
<i>Candida</i> sp.	Pretreated textile	Physical adsorption	[182]
<i>Thermomyces lanuginosus</i>	Polyurethane foam	Covalent bonding	[183]
<i>Penicillium expansum</i>	Resin D4020	Physical adsorption	[184]
<i>Thermomyces lanuginosus</i>	Styrene-divinylbenzenecopolymer	Covalent bonding	[185]
<i>Enterobacter aerogenes</i>	–	Covalent bonding	[186]
<i>Rhizopus oryzae</i> and <i>Candida rugosa</i>	Silica gel	Covalent bonding	[187]
<i>Penicillium camemberti</i>	Epoxy-SiO ₂ -PVA	Covalent bonding	[188]
<i>Candida antarctica</i>	κ-carrageenan	Entrapment	[189]
<i>Candida antarctica</i>	Silica aerogel	Entrapment	[190]
<i>Candida antarctica</i>	Celite supported sol-gel	Entrapment	[191]
<i>Penicillium expansum</i>	–	Cross-linking	[192]
<i>Staphylococcus haemolyticus</i>	Poly (methacrylate-co-divinyl benzene)	Physical adsorption /entrapment	[193]
<i>Pseudomonas cepacia</i>	Polyacrylonitrile	Physical adsorption	[194]

enzyme aggregates of *Photobacterium lipolyticum* lipase M37 with free lipases and found that the stability increases remarkably in the case of cross-linked enzyme aggregates of *Photobacterium lipolyticum* lipase M37. Cross-linking reactions are generally carried out under comparatively rough states. For example, cross-linking substances can replace the conformation of lipases which leads to a notable loss of activity. Again, in the course of cross-linking immobilization method, low yields are obtained with no advantageous mechanical properties. Therefore, lipase can be immobilized through a hybrid process which can enhance stability along with mechanical properties [206–209].

In recent times, some novel methods of immobilization are being introduced. These novel methods intensify the production of immobilized lipase, solvent forbearance, recyclability, and reliability and make the detachment procedure uncomplicated. The novel lipase immobilization

methods for the production of biodiesel are protein-coated microcrystals (PCMC), cross-linked protein-coated microcrystals (CL-PCMC), magnetic particle carriers, and electrospun nanofibers [210]. Advantages of PCMC are moderate constraint in mass transfer, great stability, and activity of the catalyst, recyclability, etc. Raita et al. [211] reported immobilization of commercial lipase obtained from recombinant *Aspergillus*. They performed biodiesel synthesis using palm olein and PCMC-lipase as a catalyst in presence of ethanol. A biodiesel yield of 89.9% was obtained within 24 h of reaction. PCMC lipase was reusable for up to 8 cycles without losing its activity. In organic solvents, PCMC-lipase exhibited high catalytic activity, but the catalytic activity was affected by partial miscibility and this might be due to the presence of water in the reaction mixture. Compared to PCMC, CL-PCMC exhibited a better catalytic activity in the case of feedstocks like WCO and microalgal

lipids. Yan et al. [209] investigated the catalytic efficacy of *Geotrichum* sp. lipase covered on K_2SO_4 (PCMC) and glutaraldehyde treated CL-PCMC in the reaction of WCO to produce biodiesel. The PCMC could produce 69% yield, whereas CL-PCMC exhibited 72% biodiesel yield [209]. The advantage of magnetic nanoparticles immobilized lipase is a simple separation and can be gathered at a particular area in a reactor by using external magnetic fields [144]. At ORCs, biodiesel yield of 70% was produced from olive oil in presence of *Burkholderia* lipase catalyst which was immobilized onto hydrophobic magnetic particles [212]. Tran et al. [213] reported that *Burkholderia* sp. immobilized onto alkyl grafted Fe_3O_4 - SiO_2 magnetic particle was utilized as a catalyst for direct transesterification of wet microalgal (*Chlorella vulgaris* ESP-31) biomass and *C. vulgaris* ESP-31 extracted lipids. This resulted in 97.3% biodiesel conversion from direct transesterification and 72.1% from transesterification of extracted oil [214]. Through the electrospinning method, nanofibrous membranes made are utilized for lipase immobilization [194,214]. Nanofibrous membrane comes up with a wide surface area for enzymatic extension and good porosity for substrate dispersion. Electrospun nanofibers are possibly applied either to adsorb lipase on the outside or to enclose it in nanofibers material. Electrospun polyacrylonitrile fibers are frequently used to immobilize lipases due to their utilization in the production of biodiesel [194,214]. By covalent attachments, *P. cepacia* lipase was immobilized on polyacrylonitrile nanofibers and used as a catalyst in the soybean oil alcoholysis reaction, and the biodiesel yield of 90% was obtained [214]. In this study, the stability of immobilized lipase nanofibers retained 91% of initial conversion even after 10 reaction cycles.

7. Comparison of enzyme-catalyzed biodiesel synthesis

The immobilized lipase can catalyze both esterification and transesterification reactions of FFA and triglycerides under mild reaction conditions, and produce good yield and good quality of by-product. The process uses low energy and generates no wastewater. The immobilized lipases could be used for several cycles of reaction. However, the disadvantages of enzymatic reactions in biodiesel synthesis are the slow rate of reaction, inhibition caused by alcohol and high price of enzymes [215,216]. Methyl and ethyl acetates are the esters and act as acyl acceptors for the synthesis of biodiesel. Usage of these esters does not have a negative impact on the activity of lipase compared to alcohols such as methanol and ethanol. Methyl and ethyl acetates do not produce glycerol in the process but a higher value side-product is obtained. However, acyl acceptors are costly [215]. The advantages of the adsorption immobilization method are easy and mild operation conditions, low-cost carrier, no need for chemical additives, high activity recovery of lipase and easy revival of carriers for reusing [132,136]. However, the disadvantages of immobilized lipase via adsorption technique are weak interaction between the carrier and lipase, and weak adsorption capacity. The immobilized enzyme is sensitive to temperature, pH and ionic strength. The immobilized lipase via covalent bonding has good stability due to strong binding between the carrier and protein, and almost no leaching of lipase is found in the transesterification process. However, the covalent bonding technique proceeds through rigorous preparation conditions and the loss of lipase activity may arise during the process. Cross-linking based immobilized lipase is stable due to strong interaction between the carrier and the lipase. The disadvantages of cross-linking based immobilized lipase are its rigorous preparation conditions that lead to activity loss and it has low mechanical strength and low yields of immobilization. The slow rate of biodiesel conversion is observed with entrapped lipases and shows weak stability.

8. Economic viability of enzyme-catalyzed biodiesel synthesis

Biodiesel production through enzyme catalysis attracts a lot of research from the scientific community and the biodiesel industry.

Recently, novel techniques are initiated to make enzyme catalysis economically viable and sustainable. The choice of inexpensive, easily available, reusability, and long-term workable biodiesel feedstocks becomes a crucial step towards the economically viable and sustainability of the biodiesel production process. The main objectives of these issues are of decreasing the cost of enzyme catalysis and improving the biodiesel conversion efficiency as well. The economic viability mainly depends on raw material cost i.e. the price of oil feedstock, alcohol, enzyme, and processing parameters such as oil to alcohol ratio, reaction time for transesterification, biodiesel yield, the lifetime of lipase, loss of solvent, by-product credit, heat integration and water recycle process design [132,217]. Moreover, the side-product glycerol produced along with biodiesel can give some profits as enzyme-catalyzed methods minimize the purification steps and improve the quality of glycerol [156]. The US environmental protection agency (EPA) has distinguished biodiesel and ethanol to be the most appropriate biofuel [218]. Moreover, immobilization can improve the stability of enzymes and permit their reusability numerous times, resulting in better performance and economic viability. In the future, its broader application may be further vitalized by the emerging bio-based economy [219]. Improvement of properties such as stability under non-natural conditions has made it possible to predefine the minimum parameters necessary for a process to be economically viable [220]. Lipase with high tolerance in temperature, organic solvent, pH, and mechanical stress perhaps promotes enzymatic biodiesel production to a more economically feasible industry. Enzyme manufacturers and biodiesel producers have cooperated recently to begin new technology of enzymatic biodiesel production to make it more feasible and economically viable [221]. The production cost of biodiesel obtained using different catalysts is summarized in Table 4. Karmee et al. [223] investigated the production cost of biodiesel from WCO using lipase, acid and base catalysts via the transesterification process. They reported the biodiesel synthesis cost of 1047.97 USD/t for lipase-catalyzed, 750.38 USD/t for acid-catalyzed, and 868.60 USD/t for base-catalyzed reaction. The higher cost of the lipase-catalyzed biodiesel synthesis process is due to the higher price of the lipase. Budzaki et al. [222] also reported a higher biodiesel cost (0.71 USD/L) of the enzyme-catalyzed process compared to base-catalyzed processes [234,235,237], and this may also be due to the higher cost of the enzyme. However, the production cost can be reduced further through proper optimization of the process parameters, and the applications of the machine learning techniques and appropriate reactors will be useful in this regard [25,146,238].

9. Conclusion and future perspectives

Chemical conversion of oil to biodiesel is an extensively used method on a laboratory and industrial scale. Biodiesel synthesis from triglycerides via transesterification or esterification is mainly affected by a load of enzyme catalyst, MTOR, reaction temperatures, and times. The enzyme catalysts are found to be active in the reaction of oil, producing biodiesel with mild reaction conditions e.g. low reaction temperature leading to higher conversion. Over chemical catalysts, lipase catalysis offers benefits such as mild reaction conditions, easy recoverability of products, good quality of biodiesel and glycerol, and no generation of wastewater.

Enzymatic reaction still needs more improvement to be utilized for biodiesel synthesis compared to chemical catalysts, and this is due to the higher cost of enzyme catalysts, lower reaction rate, and enzyme inhibition. Lipase, oil, and acyl acceptor are the three main components for biodiesel production by using enzymatic reactions. To improve biodiesel production by enzymatic transesterification, various methods have been tested such as the combination of lipase, pre-treatment of the enzyme, post-treatment of enzyme, methanol addition technique, solvent use, and addition of silica gel, which are applied to get the best yield and to decrease the effect of enzyme inhibition during transesterification process. Immobilized lipases possess high methanol tolerance,

Table 4
Summary of production cost of biodiesel obtained using different catalysts.

Country of origin	Feedstock oil	Biodiesel production process	Production Cost of biodiesel	Year of estimation ^{a*}	Reference
Croatia	Sunflower oil	Enzyme catalyzed transesterification	0.71 USD/L	2017	[222]
Hong Kong	WCO	Lipase catalyzed transesterification	1047.97 USD/t	2014	[223]
Hong Kong	WCO	Acid catalyzed transesterification	750.38 USD/t	2014	[223]
Hong Kong	WCO	Base catalyzed transesterification	868.60 USD/t	2014	[223]
India	Castor oil	Zn-CaO catalyzed transesterification	0.77 USD/kg	2020	[224]
India	Waste chicken fat	KOH catalyzed transesterification	0.392 USD/L	2015	[225]
Serbia	Sunflower oil	Base catalyzed methanolysis	0.990 USD/kg	2013	[226]
Iran	WCO	KOH catalyzed transesterification	1.201 USD/L	2012	[227]
India	Karanja oil	Base catalyzed transesterification	0.999 USD/L	2013	[228]
India	Jatropha oil	KOH catalyzed transesterification	0.536 USD/L	2012	[229]
Colombia	Palm oil	Acid catalyzed esterification and base catalyzed transesterification	0.990 USD/L	2013	[230]
Spain	Lipid	Acid catalyzed esterification/ transesterification	1232 USD/t	2016	[231]
India	WCO	NaOH catalyzed transesterification	0.752 USD/kg	2017	[232]
Brazil	WCO	NaOH catalyzed transesterification	0.1318 USD/L	2017	[233]
India	<i>Calophyllum inophyllum</i> oil	Zn-CaO catalyzed transesterification	0.68 USD/kg	2020	[234]
India	Used cooking oil	KOH catalyzed transesterification	0.407 USD/L	2018	[235]
Europe	Rapeseed oil	Transesterification	0.75 USD/L	2020	[236]
Indonesia	Palm oil	Transesterification	0.68 USD/L	2020	[236]
Portugal	Microalgae oil	Alkali-catalyzed transesterification	0.275 USD/L	2020	[237]

^{a*} Year of manuscript received for publication or year of analysis.

high catalytic efficiency, and good protection against harsh conditions and can keep their efficiency even after their many uses. The addition of methanol stepwise and separation of glycerol are the main features that can be included for more improvement of the design. For biodiesel production, the method that can be utilized in the industry for large-scale production of biodiesel needs to be improved and this may contribute toward a greener and environmentally benign energy production. Recently, the generation of lipase-inorganic HNFs exhibited good catalytic activity, stability, and reusability, and these would be excellent catalysts for biodiesel synthesis. Enzyme catalysts could be employed as an economical and more eco-friendly catalyst for the production of biodiesel than chemical-based catalysts. Also, enzyme-based catalysts would significantly contribute to overall waste minimization. In novel green solvents such as ionic liquids, lipases have shown higher stability and conversion ability, which could effectively replace toxic organic solvents to make the biodiesel production process safer. Hence, this enzymatic conversion method is a promising alternative to the conventional conversion method.

In the future, more research needs to be done in this area to explore the more efficient and highly active enzyme catalysts. Utilization of hybrid oil (mixed oil) needs to be emphasized to meet the biodiesel feedstock shortages along with the development of a chain system that

could supply the raw feedstocks continuously. Efficient reactor needs to be identified and latest machine learning techniques could be applied to model and optimize the process parameters to reduce the overall production cost. Renewable biodiesel production by an eco-friendly process i.e., enzymatic transesterification makes the overall process sustainable for future needs of clean energy. Yet many other new consequences and materials are to be developed from enzyme catalysts for sustainable applications. Therefore, considering the high potentiality of enzyme catalysts, more noteworthy contributions and progress in sustainable developments are expected in the near future.

Declaration of interests

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

CRedit authorship contribution statement

Pinaki Kalita: Conceptualization, Investigation, Writing – original draft. **Bidangshri Basumatary:** Writing – review & editing. **Pankaj**

Saikia: Writing – review & editing. **Bipul Das:** Writing – review & editing. **Sanjay Basumatary:** Conceptualization, Investigation, Methodology, Supervision, Writing – review & editing.

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