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Impact analysis of biodiesel production parameters for different catalyst

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Abstract

Catalysts play a major role in the transesterification process. In recent years, heterogeneous catalysts have gathered attention due to the advantage of reusability and easy separation. The use of renewable sources for catalyst preparation has advanced the use of heterogeneous catalysts. The biomass-derived catalysts are important in decreasing the cost of production and promoting the commercialization of biodiesel. Various renewable sources such as sea sand, shells, fish bones, large-scale industrial wastes can be used for catalyst preparation. Catalysts prepared from these wastes can make the transesterification reaction more sustainable and cost-effective. Thus, this work comprises a review of the advancements of various catalyst technologies used in biodiesel production, including the use of waste biomass for catalyst preparation. The paper also discussed the Bimetallic and trimetallic heterogeneous catalysts for several applications in energy and biodiesel generation from microalgal lipids.

Keywords Catalyst · Biodiesel · Heterogeneous · Waste-biomass · Sustainable

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1 Introduction

The growth of the world and its well-being is directly reliant on energy growth. Rapid urbanization and industrial evolution have increased the high demand for energy worldwide [1, 2]. Hence, energy plays an important role in supporting our economic and social growth [3, 4]; however, the growing energy requirements and limited reserves make it difficult. Thus, it is a serious concern to develop alternative energy sources to meet the rising energy demand. The world energy consumption from 2008 to 2018 is shown in Table 1.

As shown in Table 1, it can be observed that there is a continuous increase in energy consumption per year which is making world energy security a tough task. Figure 1 shows our over-dependency on fossil fuels. This over-dependency is causing the depletion of fossil fuels. This depletion can lead us to fail to meet the energy demand in upcoming years. Besides energy security, the burning of fossil fuels also causes high harmful gaseous emissions that affect the environment and human beings [6, 7, 8].

Thus, there is a high need to work for alternative energy sources so as to meet the energy demand and control the pollution in upcoming years [9, 10]. Considering these problems,

Table 1 Energy consumption (MT oil equivalents) [5]

Regions	Year		Growth rate per annum			
	2008	2018	2008–2018 (%)	2018 (%)	2019 (%)	Share 2019 (%)
North America	2751.0	2832.0	0.2	2.8	− 1.0	20.0
South and Central America	600.8	702.0	1.3	0.3	0.3	4.9
Europe	2173.3	2050.7	− 0.7	0.03	− 1.1	14.4
CIS	844.7	930.5	0.9	4.4	− 0.3	6.7
Middle East	653.7	902.3	3.2	2.4	3.15	6.6
Africa	365.4	461.5	2.4	2.9	2.5	3.4
Asia Pacific	4316.2	5985.8	3.3	4.1	3.3	44.1
The world	11,705.1	13,864.9	1.6	2.9	1.3	100

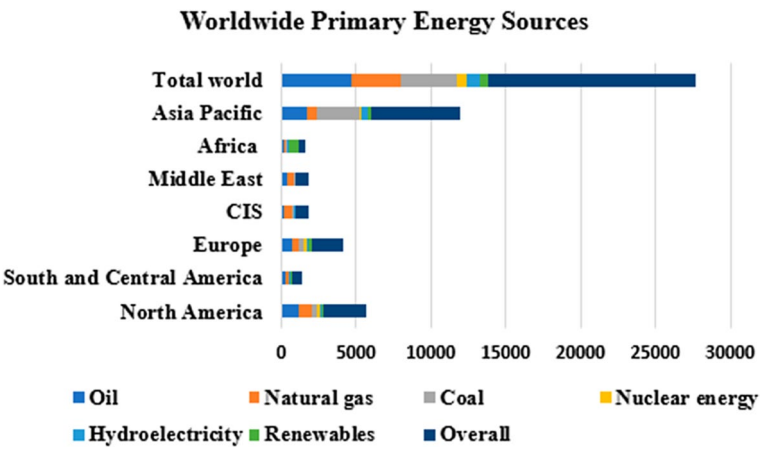

Fig. 1 Primary energy sources (MT oil equivalent) [5]

various researchers, industrialists, and world leaders are efficiently promoting energy sustainability. The only way is to maximize the use of alternative sources of energy.

This research aims to examine the technical and economic aspects of the various types of catalysts used in biodiesel production. It includes a thorough examination of the latest developments in various biodiesel catalyst technologies, including waste biomass for catalyst manufacturing. In addition, Bimetallic and trimetallic heterogeneous catalysts for energy and biodiesel synthesis from microalgal lipids were also studied in the article.

1.1 Biofuel production

Fuels derived from biomass have been promising alternatives due to their renewable nature and less exhaust emissions [11, 12]. Therefore, among different biofuels, biodiesel has gained attention all over the world. Various processes produce biodiesel, but transesterification is the most commonly used [13, 14]. Figure 2 shows the procedure of biodiesel production from two methods using different catalysts.

In Fig. 3, an increasing trend in biodiesel production can be observed worldwide. This is because the transport sector has been proved the most energy-consuming and emission-producing sector globally. Hence, biodiesel has been promoted as an alternative to petroleum due to its biodegradability [18].

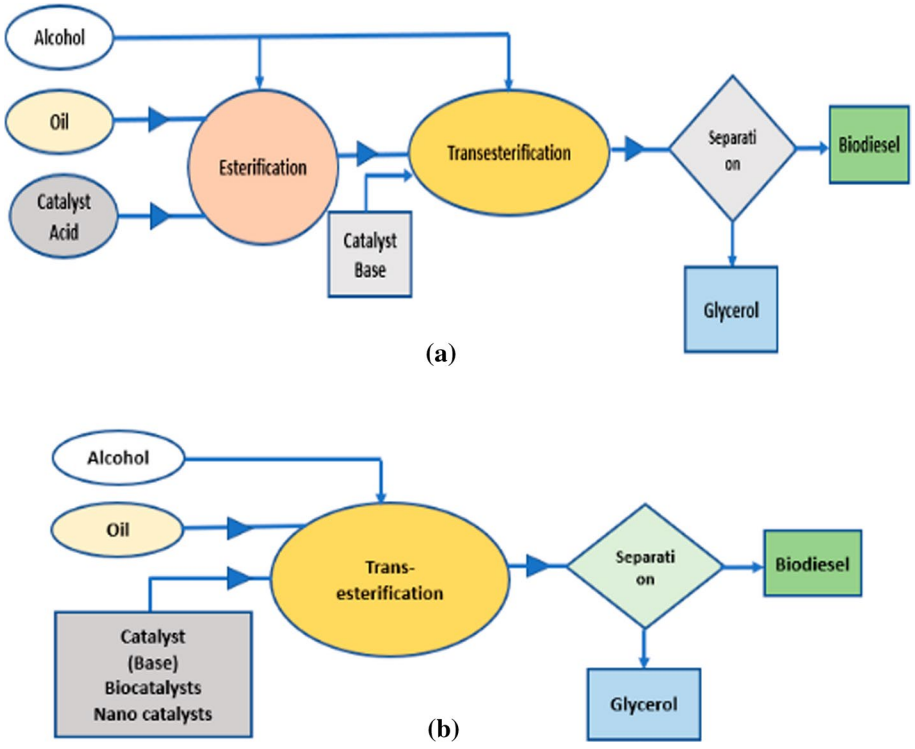

Fig. 2 Biodiesel generation procedure using different catalysts from feedstock: **a** dual step procedure [15] and **b** single step procedure [16]

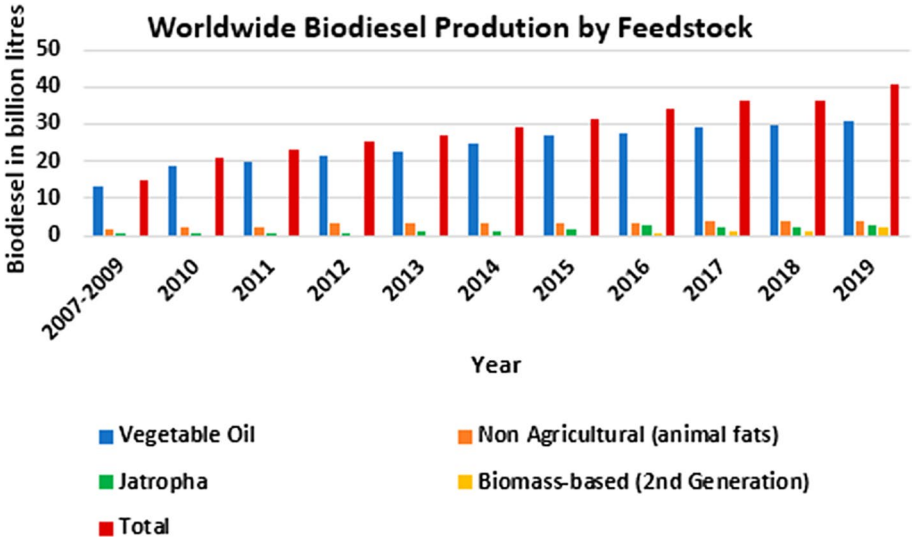

Fig. 3 Worldwide biodiesel production by various feedstock [17]

Biodiesel is a fatty acid alkyl ester produced from vegetable oils and animal fats. There are four common methods to produce biodiesel like micro-emulsification, blending, thermal cracking, and transesterification. Transesterification is the method given more attention to producing biodiesel by various researchers as it produces biodiesel with good fuel properties [2, 19]. In transesterification reaction, triglycerides react with alcohol in the presence of a catalyst to produce alkyl ester and glycerol as a by-product [20, 21, 22]. The process undergoes three consecutive reversible reactions, where triglyceride is sequentially converted into diglyceride, monoglyceride, and glycerol. As a result, an alkyl ester is produced at each stage.

2 Parameters affecting the reaction

Four different parameters take part in the transesterification reaction. These are catalyst concentration, methanol to oil ratio, reaction time, and reaction temperature. The catalyst is used to speed up the reaction for converting triglycerides into fatty acid alkyl ester. Initially, a lower amount of catalyst is used to get enough time to complete the reaction. On further increasing the catalyst amount, a decrease in biodiesel yield has been observed due to a decrease in the diffusion rate of the reactants [23]. Excessive use of catalyst is found to form emulsions reflecting on higher viscosity, thereby making biodiesel recovery difficult. In the case of high FFA, the esterification process is performed, which produces water as a byproduct. The water content in the reaction can decrease the catalyst's reactivity, thus affecting the biodiesel yield.

The alcohol to oil molar ratio has a significant effect on the biodiesel yield. In case of an insufficient amount of methanol, a reverse reaction occurs due to which a decrease in yield takes place. On the contrary, in the case of using excess alcohol, a higher conversion percentage takes place, which increases the yield. However, this excess methanol requires higher energy to recover the unreacted methanol after the reaction, increasing production

costs [24]. Furthermore, methanol with polar hydroxyl group results in the emulsification of glycerol and the biodiesel formed during the reaction. This aids to the backward reaction, i.e., recombination of glycerol and esters, thus decreasing the biodiesel yield. Therefore, it must be noted that the transesterification reaction is reversible, and therefore a large amount of alcohol is required to keep the reaction in the forward direction.

Biodiesel yield is generally observed to increase with an increase in the reaction time. However, excess reaction time also negatively affects the biodiesel yield, resulting in a decrease in yield. This excess time also increases the energy cost. On the other hand, an increase in temperature is found to speed up the reaction, and more yield is achieved, which may be due to the reduction of oil's viscosity on increasing the temperature, resulting in better mixing of oil with alcohol and faster separation glycerol from biodiesel. The reaction time and temperature majorly depend upon the type of catalyst and the amount of catalyst used in the reaction [25, 26]. Chavan et al. [27] have reported the maximum yield for the varying amount of catalyst and reaction temperature with different feedstock; for catalyst (3 wt%) with Pongamia oil, 90% yield obtained at the reaction temperature 65 ℃, whereas the reaction temperature decreases to 50 ℃ yield decreases to below 80%.

It was observed that the reaction parameters mainly vary according to the catalyst. Thus, this work focuses on studying different catalysts used in biodiesel production and discusses various advantages and disadvantages of different types of catalysts.

3 Homogeneous catalyst

Homogeneous catalysts are the commonly used catalysts in biodiesel production. These catalysts are also used in commercialized biodiesel production as they possess high catalytic activity; however, mainly solid base catalysts are used in the reaction. Nevertheless, using the base catalyst in case of high free fatty acids in the feedstock oil, saponification occurs to prevent this; acid pretreatment is performed over the oil to reduce its FFA. This process of treating biodiesel with acid is known as esterification [28, 29, 30]. Mostly used base catalysts are potassium hydroxide (KOH) and sodium hydroxide (NaOH) [31] and acid catalysts used are sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) [32] (Table 2).

The use of homogeneous catalysts increases the production cost of biodiesel as they are non-recyclable. These catalysts also face problems in separating homogeneous phase products and increasing the amount of wastewater produced during fuel purification [46]. Furthermore, from a technical point of view, the homogeneous catalysts consume two step-process due to the presence of FFA in oils which is a time-consuming and cost-increasing factor. Therefore, there is a need to introduce recyclable catalysts that can treat the problem of high FFA, reducing the steps in the process.

4 Heterogeneous catalysts

4.1 Solid acid catalyst

In concern of various disadvantages of using a homogeneous catalyst, heterogeneous catalysts were developed. These catalysts possess various advantages over homogeneous catalysts. These catalysts are prepared from the naturally aspirated metals and their derivatives. These catalysts are reusable, recyclable, and not affected by the amount of FFA present in

Table 2 Homogeneous catalysts in Biodiesel production

Catalyst	Feedstock	Catalyst concentration	Methanol to oil ratio	Reaction time	Temperature (°C)	Biodiesel yield (%)	References
H_2SO_4 NaOH	Jatropha oil	1% (w/w) 1% (w/w)	3:7 (v/v) 3:7 (v/v)	3 h 3 h	65 50	21.2 90.1	[33]
KOH	Pongamia oil	1.43% (w/w)	11.06:1	81.43 min	56.6	98.4	[34]
NaOH	Rice bran oil	0.75% (w/w)	9:1	1 h	55	90.18	[35]
H_2SO_4 KOH	Coconut oil	0.7% (v/v) 1.5% (w/v0	0.35 (v/v) 0.4 (v/v)	60 min 60 min	60 60	98.4	[36]
H_2SO_4 NaOH	Waste Cooking oil	1% 1%	3:7 (v/v) 3:7 (v/v)	3 h 3 h	65 50	21.5 90.6	[37]
H_2SO_4 KOH	Mahua oil	1.24% 0.7%	0.32 0.25	1.26 h 30 min	60 60	98	[38]
H_2SO_4 NaOH	Neem oil	0.08% 1%	1:8	1 h	60	85	[39]
KOH	Tobacco oil	1%	20:1	30 min	60	91	[40]
NaOH	Sunflower oil	1%	6:1	2 h	60	97.1	[41]
NaOH	Linseed oil	0.5	9:1	40 min	60	95.99	[42]
CH_3NaO	Waste sunflower oil	2 wt%	12: 1	70 min	55	94.33	[43]
Potassium methoxide	*Elaeagnus angustifolia* L. seed oil	1 wt%	9:1	60 min	60	95	[44]
Sodium methoxide	*Calophyllum inophyllum* oil	10 wt%	30:1	2 h	75	94	[45]

triglycerides [47]. Thus, these can improve the overall energy consumption and reduce the time of pretreatment. Table 5 depicts various studies which show the potential use of heterogeneous acid catalysts with the process parameters in biodiesel production. The application of these catalysts obtains a high yield (Table 3).

Besides the advantages of homogeneous acid catalysts, there are certain disadvantages of using these catalysts, which must be considered when considering the catalyst. First, some catalysts possess low reactivity, which directly affects biodiesel yield. Second, they require high reaction temperature and poor reusability [63]. Finally, some catalysts of these categories have complicated preparation processes. Thus, there is a need to develop other catalysts that can tackle these disadvantages of homogeneous acid catalysts mentioned earlier.

4.2 Solid base catalyst

CaO is the most widely used alkaline metal catalyst in transesterification reactions for biodiesel production. The catalyst's reactivity depends on the calcination temperature of the catalyst, whereas the reusability depends upon the efficiency of extraction of the catalyst from pure biodiesel during the cleaning process. Therefore, these catalysts have been found to have very effective reusable properties [64, 65]. The reactivity of these catalysts is very high thus, resulting in high biodiesel yield. In addition, these catalysts possess high catalytic life and are non-corrosive in nature. Table 4 depicts various studies performed by researchers using the solid base catalyst for biodiesel production from different feedstocks and their impact on other process parameters in Table 6.

Unlike heterogeneous acid catalysts, these catalysts are highly sensitive to the amount of water and FFA present in the feedstock oil. FFA requirement is less than 1%. The have a slow reaction rate compared to homogeneous catalysts, and in some cases, saponification occurs, resulting in degradation in the quality of biodiesel produced. The preparation method is also complex and expensive [85].

Besides the advantage of catalyst reusability, the high cost of biodiesel production is still a serious concern. The naturally aspirated metals present in the catalyst increase the cost of the catalyst as well as the process. Thus, there is a need to focus on eco-friendly methods to prepare the catalysts from renewable sources to be economical and less energy-consuming.

4.3 Heterogeneous catalyst derived from waste biomass

On considering problems with natural heterogeneous-based catalysts, researchers worldwide have worked for alternate sources for catalysts preparation. The new method of catalysts was developed by using lignocellulosic waste biomass and converting it into value-added products, i.e., heterogeneous catalysts. These catalysts are prepared from various types of biomass. Tables 5 and 6 depict various catalysts prepared from different types of feedstocks for transesterification reaction. This can help in reducing the cost of biodiesel production and can promote the commercialization of biodiesel.

4.3.1 Solid base catalyst from waste biomass

These catalysts are mainly prepared by direct calcination of biomass and integrating biomass with existing CaO catalysts. CaO was found one of the most widely used and promising heterogeneous base catalysts for biodiesel production [86]. Table 7 depicts various

Table 3 Heterogeneous acid catalyst

Catalyst	Feedstock	Catalyst concentration	Methanol to oil ratio	Reaction time	Temperature (°C)	Biodiesel yield (%)	References
$Fe(HSO_4)_3$	Waste oil	1 wt%	15:1	4 h	205	94.5	[48]
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Soyabean oil	3 wt%	20:1	10 h	200	90.4	[49]
Nb_2O_5/SO_4	Palm oil	30%	120:1	4 h	250	99	[50]
SO_4^{2-}/ZrO_2	*Jatropha curcas* oil	7.61 wt%	9.88 mol/mol	4 h	150	90.32	[51]
$Al(HSO_4)_3$	Waste vegetable oil	0.5 wt%	16:1	50 min	220	81	[52]
$SO_4^{2-}/SnO_2–SiO_2$	*Moringa oleifera* oil	3 wt%	1:19.5	150 min	150	84	[53]
WO_3/ZrO_2	Used vegetable oils	0.2 wt%	19.4:1	140 h	75	65	[54]
$Cr_2O_3/Na_2Cr_2O_3/Al_2O_3$	Microalgal lipids	15%	20:1	4 h	80	98.28	[55]
$SO_4/Mg–Al–Fe_3O_4$	Waste cooking oil	4 wt%	9:1	5 h	95	98.5	[56]
SnO_2/SiO_2	Soybean oil	5 wt%	24:1	5 h	180	81.7	[57]
SrO/La_2O_3	Oleosa oil	1.5 wt%	14:1	40 min	60	97.5	[58]
$Ca_2Al_2O_5$	Waste vegetable oil	1.2 wt%	6:1	25 min	56	98.7	[59]
GR-SO3H	Palm oil	10%	20:1	10 h	100	98	[60]
SO3H@ZrP	Oleic acid	5%	9:1	5 h	65	89	[61]
b-K2Zr2O5	Waste frying oil	4 wt%	10:1	2 h	65	96.8	[62]

Table 4 Heterogeneous solid base catalyst

Catalyst	Feedstock	Catalyst concentration	Methanol to oil ratio	Reaction time	Temperature (°C)	Biodiesel yield (%)	References
$CaO{\cdot}Al_2O_3$	Algae oil	1.56% (w/w)	3.2:10 (v/v)	125 min	50	88.89	[66]
CaO–NiO	Jatropha oil	5 wt%	15:1	6 h	65	86.3	[67]
Li–CaO	Karanja oil	5 wt%	12:1	1 h	65	> 99	[68]
KOH (32%)/ZrO2-5	*Silybum marianum* oil	6 wt%	15:1	2 h	60	90.8	[69]
Nd_2O_3–KOH	Soyabean oil	6 wt%	14:1	1.5 h	60	92.41	[70]
K_2CO_3/Al–Ca–25–650	Soyabean oil	2 wt%	13:1	2 h	65	95.1	[71]
NaK (20) TNT	Soyabean oil	1 wt%	20:1	1 h	80	96.2	[72]
CaO.KBr	Waste cooking oil	3 wt%	12:1	1.8 h	65	82.48	[73]
$Ca_{12}Al_{14}O_{33}$/CaO	Rapeseed Oil	6 wt%	15:1	3 h	65	90	[74]
Sr/MgO	Soyabean oil	5 wt%	12:1	30 min	65	93	[75]
$SrTiO_3$	Madhuca indica oil	1.3 wt%	18:1	120	65	98	[76]
$K_2Al_2O_4$	Kusum oil	1 wt%	15:1	90	65	97.08	[77]
La_2O_3	Castor seed oil	2 wt%	16:1	150	65	97.5	[78]
$BaCeO_3$	Karanja oil	1.2 wt%	19:1	100	65	98.4	[79]
K/ZnO	Algal oil	1.5 wt%	16:1	60	65	97.5	[80]
Mixed metal oxide of Ba–Ca–Z	Spirulina platensis	2.5 wt%	18:1	120	65	98.8	[81]
Sr–Ce mixed metal oxide	Waste cooking oil	2 wt%	14:1	120	65	99.5	[82]
Barium lanthanum oxide	Mahua oil	2 wt%	16:1	150	65	97.5	[83]
Potassium impregnated ZnO	Waste cooking oil	2.5 wt%	18:1	90	65	98	[84]

Table 5 Base catalyst from biomass

Catalyst	Biomass	Feedstock	Catalyst concentration	Methanol to oil ratio	Reaction time	Temperature (°C)	Biodiesel yield (%)	References
CaO	Chicken egg shell	*Chlorella vulgaris*	1.39%	10:1	3 h	70	92.03	[87]
C2(4 wt% CaO)	Waste date pits	Date pits oil	4.5	12:1	2 h	70	98.2	[88]
6 wt% KOH on carbon	Waste date pits	Date pits oil		9:1	1 h	65	91.6	[89]
Biochar with 25 wt% K_2CO_3	Waste pomelo peel	Palm oil	6 wt%	8:1	2.5 h	65	98	[90]
4Mn–6Zr/CaO	Waste egg shell	Waste cooking oil	3 wt%	15:1	3 h	80	92.1	[91]
Activated biochar 600	Waste cork	Waste cooking oil (canola oil)	1.5 w/v%	25:1	6 h	65	98	[92]
Murmuru kernel shell biochar- SO_3H	Murmuru Kernel shell	Jupati oil	6%	30:1	4 h	135	91.8	[93]
CaO	Waste egg shell	Rapeseed oil	4%	9:1	1 h	60	96.81	[94]
Tucuma peel ash catalyst	Waste tucuma peels	Soyabean oil	1 wt%	15:1	4 h	80	97.3	[95]
CaO	Eggshells	Rubber seed oil	5 wt%	9:1	4 h	65	97.84%	[96]

Table 6 Acid catalyst from biomass

Catalyst	Biomass	Feedstock	Catalyst concentration	Methanol to oil ratio	Reaction time	Temperature (°C)	Biodiesel yield (%)	References
Jatropha seed cake	De-oiled *Jatropha curcas*	Jatropha curcas oil	7.5 wt%	12:1	1 h	60	99.13	[98]
BSY-SO_3H	Brewer spent yeast	Palm oil distillate	8 wt%	21:1	3 h	65	87.8	[99]
CCS-DS-SO_3H	Coconut coir husk	Waste palm oil	10 wt%	12:1	3 h	130	89.8	[100]
ZrO_2/BLA	Bamboo leaf ash	Soyabean oil	12 wt%	15:1	30 min	50	92.75	[101]
Orange peel activated carbon-SO_3H	Waste orange peels	Corn acid oil	5%	19.95:1	274 min	65	91.68	[102]
Sulfonated carbon catalyst	Shell of mesua ferrea seeds	Mesua ferrea oil	10 wt%	6:1	2 h	55	95.57	[103]
Sulfonated alkali lignin	Olive cake	Sunflower oil	10 wt%	35:1	6 h	65	57	[104]
Sulfonated carbon catalyst	Coconut shell	Palm oil	6 wt%	30:1	6 h	60	88.03	[105]
Palm kernel shell-SO_3H	Palm kernel shell	Palm fatty acid distillate	4 wt%	15:1	1 h	65	95	[106]
Bamboo-SO_3H	Bamboo	Palm fatty acid distillate	4 wt%	15:1	1 h	65	94.2	[106]

Table 7 Benefits and drawbacks of various types of catalysts [16]

Types of catalyst	Benefits	Drawbacks	Sample catalyst
Homogeneous acid catalyst	Powerful catalytic action Acceptable for feedstock with excessive free fatty acid No soap formation	The reaction rate is slower compared to the base catalyst Separation and reuse unusual Corrosion problem	Hydrochloric acid, Sulfuric acid, Sulfonic acid,
Homogeneous base catalyst	Powerful catalytic action Cheap and widely available No corrosive Ideal for thermogravimetric analysis with low free fatty acid	Possible formation of soap Not suited for feedstock with high free fatty acid No reusability Requires extensive washing	Hydroxide of Sodium or potassium; Methoxides of Sodium and potassium, Sodium and Potassium carbonates
Heterogeneous base catalyst	Easy purification of the product Minimum Effluent generation Catalyst can be reused	High cost to synthesize catalyst Leaching of active sites may occur	Alkaline earth and alkali metal oxides, transition metal oxides, mixed metal oxides, hydrotalcite
Heterogeneous acid catalyst	Easy to separate Catalyst can be reused	High cost to synthesize catalyst Higher alcohol-to-oil molar ratios High catalyst concentrations Longer reaction time May undergo deactivation	Cation exchanges reins, heteropoly acid derivatives, sulfated oxides, sulfonic acids

heterogeneous base catalysts developed from different feedstocks of biomass. These catalysts possess low surface reactivity, thus are integrated with other compounds to increase the reactivity and improve the biodiesel yield. As mentioned in above section, these base catalysts require low FFA oil for the transesterification reaction. Otherwise, there might be the formation of soap during the process. That means a pretreatment of oil is required in the process.

For further improvement in the performance of biomass CaO catalysts, researchers developed another method of integrating biomass with CaO. Researchers have limited the use of available CaO catalysts. Instead, more emphasis is provided on the CaO production from calcination of waste biomass [25]. Thus, various studies have been proposed o biomass-derived CaO and biomass as supporting materials for CaO.

4.3.2 Solid acid catalyst from waste biomass

The most common method for preparing acid catalysts is the sulfonation method comprising direct sulfonation by thermal treatment of carbon material concentrated with H_2SO_4. These carbon materials are produced from waste biomass. These catalysts are ineffective of high FFA present in triglycerides of oils. This sulfonation process helps in high biodiesel yield at the low reaction temperature. However, the corrosive behavior of H_2SO_4 has limited the use of solid acid catalysts [97].

4.4 Bimetallic and tri metallic catalyst

Nowadays, bimetallic and trimetallic heterogeneous catalysts have been examined for a variety of applications in energy and Biodiesel production and be used for environmental remediation. These catalysts have tunable properties that is controlled by their metallic compositions, morpho structure, and preparation method [107]. The performance of some bimetallic catalysts such as Au–Ag, Ca/Fe, Al–MCM-41, Ni–W, Mo–Zn, Mo–Mn, Mo–Sn supported on mixed metal oxide, W–Zr/CaO have been evaluated by different authors [82, 108, 109, 110] for the efficient production of biodiesel. However, few trimetallic heterogenous catalyst offered better catalytic properties over the mono and bimetallic catalyst. Abdulkareem et al. [111] experimentally reported the catalytic performance of Fe–Co–Ni predominates over Fe–Ni, Fe–Co, Ni–Co or their monometallic form. In addition to mono, bi and tri metallic catalyst, some ternary and quaternary metal compound such as Cu/Zn/Ca/Al_2O_3 and Cu/Ni/Ca/Al_2O_3 are also competent to produce methyl esters with greater yield and quality [112].

4.5 Catalysts used for biodiesel synthesis from microalgae

As the demand for oil crops increases for human consumption, it is not desirable to use oil crops for biofuel production. Hence, the researchers and scientists focused on alternative oil source lipids that contain aqua biomass in terms of microalgae or macroalgae. The application of microalgae over macroalgae toward biodiesel production has several advantages such as higher growth rate (doubling in 24 h); higher yield (15–300 times) as compared to the conventional oil crops in area wise; harvesting is also possible multi times in a year; they are highly biodegradable and nontoxic. Biodiesel can be made from the esterification and transesterification of a variety of microalgal/macroalgal lipids (such as Chlorella protothecoides, Oedigonium and Spirogyra) and an alcohol with the help of a

catalyst [113]. Several homogenous catalysts such as sulfuric acid or sodium hydroxide used with methanol due to their high reaction at low temperature and atmospheric pressure. In addition to the homogenous catalysts, various heterogenous catalysts such as alumina supported calcium oxide and magnesium oxide, H-Beta zeolite, calcium methoxide, chromium–aluminum mixed oxide [114] are also used to produce methyl ester biodiesel from *Nannochloropsis oculate*, *N. gaditana*, *Scenedesmus obliquus* and *Spirulina* sp. microalgal lipids, respectively [113].

5 Economics of biodiesel

Several important factors drive the economics of biodiesel production and its feasibility in a practical world. First, government policies play a critical role in the biodiesel economy. Over the last decade, biodiesel production and usage have increased substantially with the involvement of governments and non-profit organizations in the form of biofuel mandates, subsidies to user groups and production companies, tax advantages, and compulsory targets. In the initial stages, vegetable oil feedstock was used for biodiesel production due to its principal usage for food and high cost. Hence the focus has been shifted to produce biodiesel from waste stream feedstock such as non-edible oils, micro-algae, waste plastics, and waste tyres. Thus, the major factors that influence the economics of biodiesel are crude oil prices, the production cost of feedstock, market requirements, and government contribution in the form of tax subsidies. Biodiesel made from microalgae has become a viable alternative to traditional feedstock in terms of industrial production and commercialization. Microalgae have a high rate of growth and carbon sequestration and can be easily grown in fresh and/or marine water without the use of arable soil. The cost of producing microalgae biodiesel is 0.38 USD per litre [115], which is commercially viable over a 10-year period when considering the economic value of residual biomass and glycerol by-products.

6 Major findings

The significant findings based on the current study are appended as follows:

- Potassium hydroxide (KOH) and sodium hydroxide (NaOH) are the most commonly used base catalysts, while sulfuric acid (H_2SO_4) and phosphoric acid are the most commonly used acid catalysts (H_3PO_4).
- In the transesterification reaction for biodiesel production, CaO is the most extensively utilized alkaline metal catalyst among KOH (32%)/$ZrO_{2\text{-}5}$, Nd_2O_3–KOH, Sr/MgO, $BaCeO_3$, and $K_2Al_2O_4$.
- Alternative catalyst preparation sources have been sought by researchers all around the world. The new catalytic approach was created by turning waste lignocellulosic biomass into value-added. Despite the benefit of catalyst reusability, the high cost of biodiesel manufacturing remains a major concern. In addition, the presence of naturally aspirated metals in the catalyst raises the cost of both the catalyst and the process. As a result, eco-friendly approaches for preparing catalysts from renewable sources must be prioritized in order for the process to be cost-effective and energy efficient.

- Bimetallic and trimetallic heterogeneous catalysts are being investigated for several applications in energy and biodiesel generation and environmental cleanup. Trimetallic Fe–Co–Ni outperforms bimetallic Fe–Ni, Fe–Co, Ni–Co or its monometallic form.
- Various heterogeneous catalysts are used to produce methyl ester biodiesel from *Nannochloropsis oculate*, *N. gaditana*, *Scenedesmus obliquus*, and *Spirulina* sp. microalgal lipids, including alumina supported calcium oxide and magnesium oxide, H-Beta zeolite, calcium methoxide, and chromium–aluminum mixed oxide.

7 Conclusions

For commercial biodiesel production, most firms employ homogenous catalysts, which causes separation and waste neutralization issues. In addition, during the purification of biodiesel, these catalysts produce a substantial volume of wastewater. Advances in heterogeneous catalysts have helped to alleviate the issues associated with homogeneous catalysts while also lowering the cost of producing biodiesel. They have a non-corrosive nature and can be reused. The use of biomass for catalyst manufacture has also advanced the preparation of heterogeneous catalysts. As a result, the transesterification reaction is processed in a green manner. These catalysts lower the transesterification process' activation energy, reducing energy consumption and reaction time. The use of biomass-derived catalysts lowers the cost of manufacturing biodiesel while maintaining a high output.

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