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Bifunctional Heterogeneous Catalysts for Biodiesel Production using Low Cost Feedstocks: A Future Perspective

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Abstract

Currently, the fossil fuel sources are the major contributors to the world's energy mix. However, these conventional energy sources are depleting very fast due to their finite nature and extensive uses. An addition to their finite nature, environmental problems related to their uses are getting progressively worse and worse, initiating challenging debates for scientific communities. Biodiesel, a renewable fuel, has shown promising prospects due to its strong socioeconomic benefits and motivations in most of the countries of the world. Bifunctional heterogeneous catalysts are strongly recommended for biodiesel production from different feedstocks to simplify the process. This review highlights the challenges and opportunities associated with the heterogeneous catalysts and some recommendations to design an efficient bifunctional heterogeneous catalyst for economical biodiesel production from waste cooking oil.

Keywords: biodiesel, bifunctional heterogeneous catalyst, recommendation

1. Introduction

Deep concerns regarding fast depletion of conventional energy resources and their associated environmental issues are hot debates for both developed and developing countries. Moreover, these conventional energy sources are located in politically unstable regions, creating issues about scarcity of supplies and instabilities in the international oil prices [1]. It is, therefore

essential to explore some alternative, potential, renewable, and sustainable source of energy that would be secure, economical, and environment friendly [2–4]. Among explored biofuels, biodiesel has received a great deal of attention as compared to other biofuels due to its domestic and renewable origin, nontoxic nature, biodegradability, environmental benefits, and excellent lubricity [5, 6].

A variety of oleo-chemical feedstocks such as vegetable oils (edible and non-edible oils), waste cooking oils (WCOs), animal fats, and greases have been identified as potential raw oils for biodiesel production in different countries (**Figure 1**) [7]. At present, biodiesel is mainly produced from edible oils all over the world (more than 95%) [8, 9]. However, the extensive use of edible oils for biodiesel production might lead to chronic food crisis in poor and developing countries. Therefore, to avoid the food problems, World Food Organization (WFO) has also legislated strict regulations over the use of edible oils for fuel purpose. The use of non-edible oils or waste cooking oils is therefore considered to be the possible solution to overcome the food issues as well as lower the biodiesel production cost-effectively [10–14]. In addition, the use of waste cooking will further solve the environmental problems that arise from its disposal [15, 16].

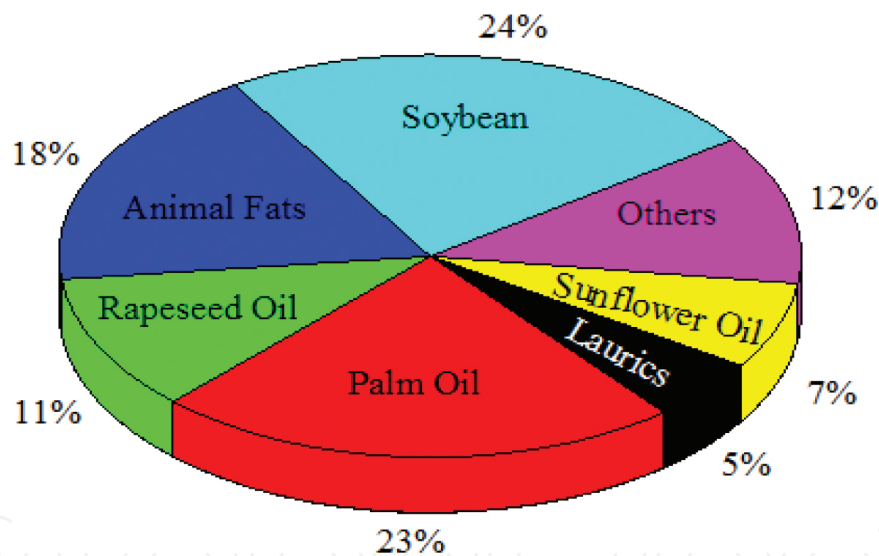


Figure 1. Production of biodiesel from different feed stocks [7].

Commercially, biodiesel production is carried out from vegetable oils or animal fats using homogeneous catalysts all over the world [17, 18]. Homogeneous base catalysts possess high catalytic activity under mild reaction conditions (from 40 to 65°C in normal atmospheric pressure) [19]. Similarly, homogeneous acid catalysts are also used in the biodiesel production from high free fatty acids feedstocks. However, homogeneous catalysts bear some technical issues such as soap formation, reactor corrosion, difficult to recover, and the production of large amount of polluted water, which in turn increase the overall biodiesel production cost and hazards [20, 21]. Therefore, special attention is being paid to the involvement of the heterogeneous catalyst for biodiesel production due to their green and recyclable catalytic

activities. Heterogeneous catalysis has the ability to mitigate the various challenges encountered with the use of homogeneous catalysts for biodiesel production from low cost feedstocks. Heterogeneous catalysts bear several technical advantages such as easy separation and purification of the reaction products, reduced reactor corrosion, low sensitivity towards free fatty acids and moisture contents [22, 23]. In general, solid base catalysts show high activity, relatively shorter reaction times, and require lower reaction temperatures as compared to solid acid catalysts [24]. However, solid acid/ base catalysts have several limitations such as feedstock specification, deactivation due to leaching, and reusability for sustainable biodiesel production.

Recently, the concept of bifunctional heterogeneous catalysts has been introduced in the biodiesel technology for efficient biodiesel production from different feedstocks. Several studies have been carried out on the use of the bifunctional heterogeneous catalyst for biodiesel production from low cost feedstocks [25–28]. Bifunctional heterogeneous catalysts exhibit both acid and base character, therefore can simultaneously carry out esterification of free fatty acids and transesterification of triglycerides to develop cleaner and economical processes for biodiesel production. More importantly, a bifunctional heterogeneous catalyst can easily be modified to introduce the desired physicochemical properties so that the presence of free fatty acids or water does not adversely affect the reaction steps during the transesterification process.

This study aims to review the role of bifunctional heterogeneous catalysts in biodiesel production from different feedstocks for a sustainable energy process. In addition, the possible recommendations will also be discussed in the light of existing problems associated with the current biodiesel technology to design a robust catalyst for a sustainable biodiesel technology.

2. Biodiesel and its production scenario

According to American Society for Testing and Materials (ASTM), biodiesel is a mixture of mono-alkyl esters of long-chain fatty acids derived from vegetable oils (edible and non-edible origin) or animal fats. Biodiesel is regarded as a clean fuel, emitting negligible amount of pollutants into the environment and sufficiently reduces the emission of pollutants when blended with diesel [29–31]. A number of methods are currently used for biodiesel production from different feedstocks to overcome the high viscosity of the vegetable oils as a fuel. However, there are four main processes employed for biodiesel production (**Figure 2**): direct use and blending of raw oils [32, 33], micro-emulsions [34, 35], thermal cracking [36, 37], and transesterification [38–40]. Among them, the most commonly used method for converting oils into biodiesel is transesterification because the fuel produced by this method shows good compatibility with the existing engine [41, 42]. The vegetable oils and fats are extremely viscous (10–17 times viscous than petroleum diesel fuel), therefore posing several problems as alternative engine fuels [43]. The main objective of the transesterification process is to lower the viscosity of the oil close to that of petro-diesel. In transesterification, vegetable oils or animal fats are chemically converted into their corresponding fatty acid esters in the presence of alcohol using a suitable catalyst [44, 45].

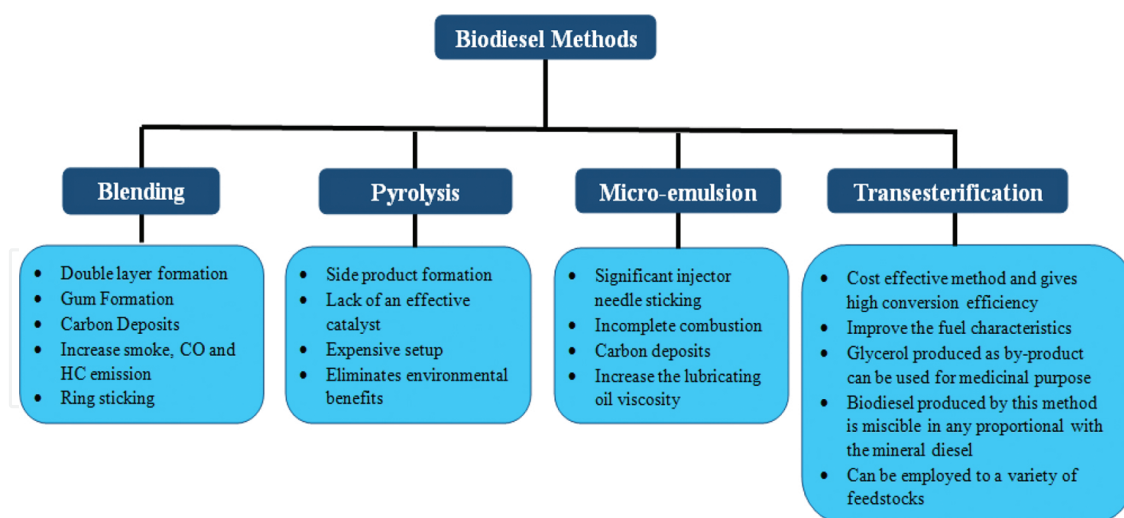


Figure 2. Methods used for biodiesel production.

The cost of biodiesel is widely regarded as a principal barrier in the development of the sustainable energy process. It has been reported that the feedstock cost is the major factor contributing to the final biodiesel cost and this cost represents approximately 70–95% of the total cost of biodiesel production [46–48]. Therefore, several efforts have been devoted to explore and select an ideal feedstock for economically viable biodiesel production. As a result, some countries of the world have focused on the use non-edible oils as a feedstock for biodiesel production to avoid food problems. However, the use of non-edible oils for biodiesel production cannot be the ultimate solution for a sustainable energy process as large plantation land areas would be required for large-scale non-edible oils production. This may disturb the entire animal and plant ecosystems [45, 47]. Therefore, it is important to search for cost effective biodiesel feedstock such as waste cooking oil, which is cheap and easily available all over the world. The utilization of waste cooking oil as a fuel effectively resolves the environmental problems associated with its direct discharge into the drainage system [49].

Similarly, another important factor contributing to the final cost of biodiesel is the technological challenge, involving exploration of highly effective catalysts and their corresponding processes for a sustainable biodiesel technology. A wide range of catalysts (homogeneous/heterogeneous) can be employed for biodiesel production from different feedstocks as shown in **Figure 3**. Heterogeneous catalysis has been considered to be the best choice for the biodiesel technology in the near future. Heterogeneous catalysts can easily be recovered, recycled, and have environmental friendly behavior. Recently, bifunctional heterogeneous catalysts have gained worldwide interest for biodiesel production due to their excellent performance in biodiesel production from low cost feedstocks. A bifunctional heterogeneous catalyst has the ability to carry out simultaneous esterification of free fatty acids and transesterification of triglycerides present in the waste cooking oil efficiently.

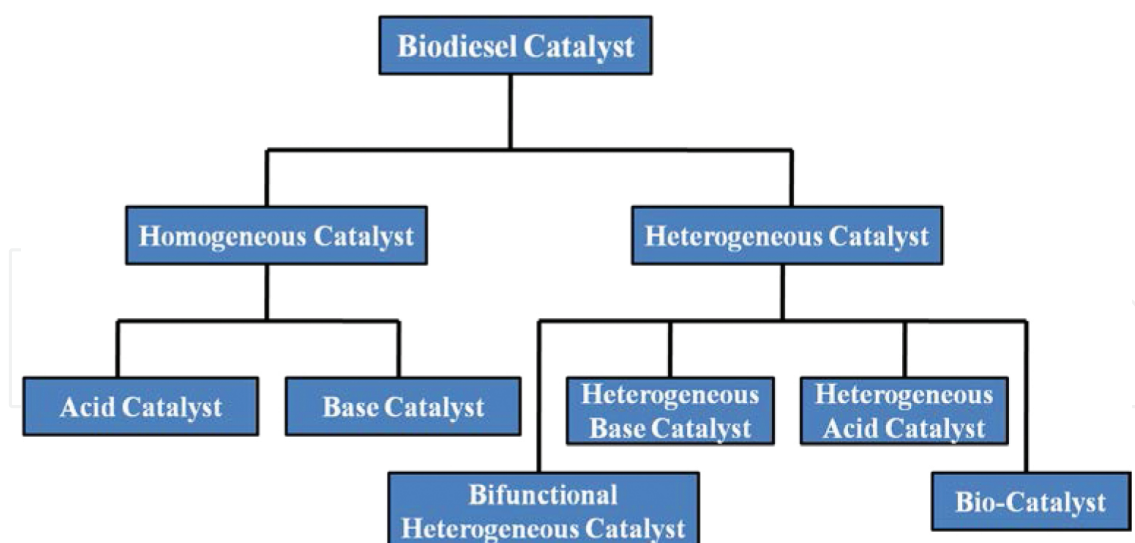


Figure 3. Catalysts used for biodiesel production.

3. Feedstocks for biodiesel production

Biodiesel is mainly produced by tranesterifying vegetable oils or animal fats commercially. However, compared to petroleum-derived diesel, the high cost of biodiesel is a major obstacle to its commercialization, which is 1.5–3 times higher than petroleum derived diesel [14]. The feedstocks mainly contribute to a major portion of the overall biodiesel production cost. Therefore, it is essential to select a feedstock for biodiesel synthesis, which is cheap, domestically available, and not compete with the food materials.

The choice of feedstocks for biodiesel production depends on two main factors, its availability and cost. Biodiesel is produced from different biological raw materials such as vegetable oils (edible and non-edible oils), animal fats, algal lipids, waste cooking oil, etc. [50–52]. Edible vegetable oils such as canola oil and soybean oil in USA, palm oil in Malaysia, rapeseed oil in Europe, and corn oil have been used as feedstocks for biodiesel production and found to be good diesel substitutes. Non-edible vegetable oils, such as oil from *Pongamia pinnata* (Karanja or Honge), *Jatropha curcas* (Jatropha or Ratanjyote) and *Madhuca indica* (Mahua) have also been found to be suitable feedstocks for biodiesel production [53, 54].

Similarly, algal lipids as feedstocks for biodiesel production are also gaining interest all over the world [55]. Algae convert carbon dioxide into sugar and proteins in the presence of sunlight. However, in the absence of nitrogen they mainly produce oil. A microalgae *Chlorella protothecoides*, has been grown under autotrophic and heterotrophic conditions to obtain lipids as a raw material for biodiesel industries. The lipid content in the heterotrophic cells reached 55.20% as compared to 14.57% in autotrophic cells [56].

Vegetable oils (edible and non-edible oils) are the predominant raw materials for the production of biodiesel, because they are renewable, potentially an inexhaustible source of energy,

possess environmentally friendly characters, and can be produced on a large scale [16]. More than 95% of the biodiesel production is made from edible oils in different countries. It has been reported that approximately 70–95% of the total biodiesel production cost is related to the cost of the raw materials (vegetable oil or animal fats) [11, 21, 22]. According to reports of Food and Agriculture Organization (FAO), esculent plants containing oil are used for the production of biodiesel among which about 84% of the biodiesel is from rapeseed oil (RSO) and the remaining is from sunflower (13%), palm oil (1%), soybean, and others (2%) [2].

Moreover, the use of edible oils for fuel production is puzzling as more and more of the global food demand rises. There are also issues of deforestation and ecological imbalance while diverting the virgin forests and arable lands to large-scale biofuel production feedstocks [57]. In other words, the sustainability of edible oils as a biodiesel feed is under threat. Thus, the biodiesel production technology faces several challenges that must be overcome to make it sustainable.

The use of waste cooking oils for biodiesel production instead of edible oils can be a promising choice to enhance the economic viability of biodiesel production on a large scale. It has been reported that the biodiesel production cost can be reduced effectively from 60 to 70% by using waste cooking oil [24]. Since waste oil is easily available at a relatively low price, therefore can be a workable feedstock for biodiesel production to make the biodiesel competitive in price with petroleum-based diesel.

Huge amounts of waste cooking oils are produced all over the world every day, especially in the developed countries. Such a large amount of waste cooking oil production can lead to several disposal problems and contamination to water and land resources and ultimately to environmental pollution. Therefore, we need to search a green utilization of waste cooking oil to avoid the disposal problems. The utilization of waste cooking oil, as feedstock for biodiesel production is not only economical and guarantees food safety but will also minimize the environmental problems associated with their disposal [58]. The estimated waste cooking oil production in the selected countries is depicted in **Table 1**. Recently, several studies have been made to investigate the biodiesel production from waste cooking oil using heterogeneous catalysts for sustainable energy production. The details of these studies are given in **Table 2**.

Country	Waste cooking oil produced (million tons/year)
United States	10.00
China	4.50
Europe	0.70–1.00
Japan	0.45–0.57
Malaysia	0.50
Canada	0.12
Taiwan	0.07
Ireland	0.153

Table 1. Annual production of waste cooking oil in the selected countries [59].

Catalyst	Time (min)	Temperature (°C)	Catalyst loading (wt%)	Methanol:oil ratio	Yield (%)	Reference
CaO	120	65	0.78	12:1	≥ 99 (soap formation occurred)	[60]
Oil Palm Ash (K ₂ O major component)	30	60	5.35	18:1	71.74	[61]
Quick Lime Bit (solid base catalyst)	120	60	1.3	150:300 (v/v)	96.5	[62]
CaO	180	60	2	7:1	≥ 80.0	[63]
CaO-La ₂ O ₃	180	58	5	20:1	~ 96.0	[64]
Mg-Al hydrotalcite	360	120	6	24:1	≥ 90	[65]
Mg-Al hydrotalcite or Mg-MCM-41	300	60	0.5	65 mL methanol and 5 g oil	97 or 87	[66]
ZnO-La ₂ O ₃	180	200	3	180:126 (wt/wt)	96	[67]
K ₃ PO ₄ (tri-potassium phosphate)	120	60	4	6:1	97.3	[68]
Zn ₃ La ₁ (Lanthanum modified Zno	180	200	2.4	26:1	92.3	[69]
CaO	120	80	3	6:1	≥ 84	[70]
Heterogeneous base catalyst						
Na-Mg-Al hydrotalcite (HT-Na)	480	60	7	9:1	67	[71]
Mg _{1-x} Zn _{1+x} O ₂	255	188	2.5	9:1	≥ 80	[72]
SrO	0.67	MW oven of 1100 output with a magnetic stirring	0.276	6:1	99.8	[73]
Mg-Al hydrotalcite (2:1)	240	65	2.5	9:1	77.2	[74]
Hydrated lime	120	60	3.6	0.17 (vol)	100	[75]
CaO-ZrO ₂	120	65	10	30:1	92	[76]
CaO (Clamshell)	180	60	3	6.03:1	> 89	[77]
KOH/Al ₂ O ₃	120	70	5	9:1	96.8	[78]
Calcined snail shell (CaO is major component)	480	65	2.0	6.03:1	87.28	[79]
CaAl ₂ -CLDH (hydrocalumite)	300	65	5	≤6:1	≥ 95	[80]

Catalyst	Time (min)	Temperature (°C)	Catalyst loading (wt%)	Methanol:oil ratio	Yield (%)	Reference
Calcined eggshell waste (99.2 wt% CaO)	4	900 W Microwave power	15	18:1	96.7	[81]
Waste mud crab shells + cockleshells + boiler ash Heterogeneous acid catalyst	30	65	3	15:1	99	[82]
$K_4Zn_4[Fe(CN)_6]_3 \cdot 6H_2O \cdot 2(t-BuOH)$ [Fe–Zn double-metal cyanide (DMC) complexes]	480	170	3	15:1	98.0	[83]
D-glucose-derived solid acid	720	80	0.5	5.54:5 (wt/wt)	≥ 90	[84]
SO_4^{2-}/TiO_2-SiO_2	120	200	3	9:1	92	[48]
Zinc stearate/ SiO_2	600	200	3	18:1	98	[85]
Starch-derived solid acid	600	80	10	30:1	92	[86]
$H_3PW_{12}O_{40} \cdot 6H_2O$ (heteropolyacid)	840	65	0.0375	70:1	97	[87]
$Al_{0.9}H_{0.3}PW_{12}O_{40}$ (aluminum dodecatungstophosphate)	840	65	3	34:1	96.1	[88]
$Zn_{1.2}H_{0.6}PW_{12}O_{40}$	720	65	2.5	28:1	97.2	[89]
$Zr_{0.7}H_{0.2}PW_{12}O_{40}$ (heteropolyacid, ZrHPW)	320	65	2.1	20:1	96.7	[90]
SO_4^{2-}/SnO_2-SiO_2	180	150	3	15:1	92.3	[91]
WO_x/Al_2O_3	120	110	1	0.3 (wt/wt)	97.5	[92]
SO_4^{2-}/ZrO_2	240	120	3	9:1	93.6	[93]
$Fe_2(SO_4)_3/C$	180	95.15	3.5	18:1	98	[94]
12-Tungstophosphoric acid (TPA)/ Nb_2O_5 (25 wt % TPA)	1200	200	3	18:1	92	[95]
SO_4^{2-}/SnO_2-SiO_2	90	150	6	15:1	88.2	[96]
Vegetable oil asphalt-based solid acid	270	220	0.2	16.8:1	94.8	[97]
$Al(HSO_4)_3$	50	220	0.5	16:1	81	[98]
Arenesulfonic acid-functionalized mesoporous silica SBA-15	120	160	8	30:1	~ 80	[99]
SO_4^{2-}/SnO_2-SiO_2	60	150	6	Methanol:ethanol:oil: 9:6:1	81.4	[100]

Catalyst	Time (min)	Temperature (°C)	Catalyst loading (wt%)	Methanol:oil ratio	Yield (%)	Reference
Silica-sulfuric acid	30	60	1.5	6:1	90	[101]
Al ₂ O ₃ ·Si ₂ ·2H ₂ O (kaolinite)	120	160	3	31:1	92.4	[102]
SO ₄ ²⁻ /ZrO ₂ -Al ₂ O ₃	240	200	0.3	67.9:1	94.8?	[103]
H ₃ PW ₁₂ O ₄₀ ·6H ₂ O	60	30 (1.3 kW reboiler duty)		67.9:1	93.98	[104]
Cs _{2.5} PW ₁₂ O ₄₀ [Cs-doped heteropoly acid]	40	260 (pressure: 20 MPa)	3	40:1	92	[105]
Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ /ionic liquids	220	70	1	6:1	97.3	[106]

Table 2. Summary of various heterogeneous catalysts used in the transesterification reaction of waste cooking oil.

The catalysts mentioned in **Table 2**, show good catalytic activity in biodiesel production from low cost waste cooking oil feedstocks. However, several problems such as separation, recycling, soap formation, leaching, reactor corrosion, etc., are associated with these catalysts while using for biodiesel production from low cost feedstocks containing high free fatty acids and water contents. In order to overcome these problems, bifunctional heterogeneous catalysts have been formulated to produce biodiesel from low cost feedstocks for a sustainable energy process. Bifunctional heterogeneous catalysts show very good efficiency in low cost feedstock conversion into biodiesel by carrying transesterification of triglycerides and esterification of free fatty acids present in the feedstock without any substantial loss in their activity due to the water content present.

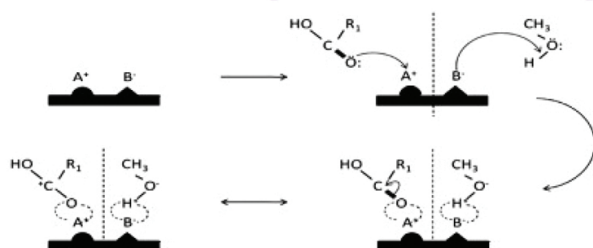
4. Bifunctional heterogeneous catalysts for biodiesel production

Several studies have been carried out to address the technical challenges associated with the biodiesel technology for large-scale and profitable biodiesel production. First, the high cost of edible vegetable oil as the source of triglycerides plays a key role in process profitability. Therefore, to reduce the biodiesel production costs and make it competitive with petroleum based diesel, low cost feedstocks, such as non-edible oils, waste frying oils, and animal fats, may be utilized as raw materials. However, the major problem associated with such feedstock is higher amounts of free fatty acids and water, resulting in soap formation in the presence of an alkali catalyst. Thus, additional steps are required in order to remove any water and either the free fatty acids or soap from the reaction mixture.

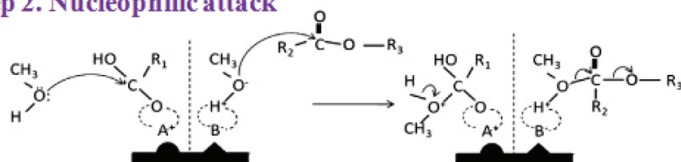
Therefore, synthesis of novel heterogeneous catalysts with desired physical and chemical properties for biodiesel production from low-grade feedstocks is one of the focuses of the catalytic scientist. In this context, the bifunctional heterogeneous catalyst with acid-base character has attained a great focus for various organic reactions over the past decade. Bifunctional heterogeneous catalysts carry out simultaneous esterification of free fatty acids

and transesterification of TG present in the oil effectively without being affected by the water content present or produced during the biodiesel formation due to the presence of both active acids and bases sites on the surface of catalyst, thereby effectively reducing the biodiesel production cost. Moreover, bifunctional heterogeneous catalysts can easily be tuned to include desired catalyst properties so that the presence of free fatty acids or water does not adversely affect the reaction steps and the biodiesel yield during the transesterification of triglycerides. The general mechanism for bifunctional heterogeneous catalysts is presented in **Figure 4**.

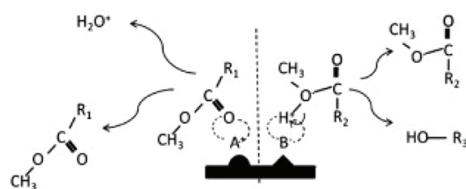
Step 1. Methanol and FFA adsorption on basic acid sites respectively.



Step 2. Nucleophilic attack



Step 3. Desorption



A⁺: Acid site on the catalyst surface
 B⁺: Basic site on the catalyst surface
 R₁: Alkyl group of fatty acid
 R₂: Alkyl group of fatty acid on triglyceride
 R₃: alkyl group of triglyceride

Figure 4. General mechanism for simultaneous esterification and transesterification reactions on bifunctional heterogeneous catalyst [107].

Several attempts have been made to investigate the catalytic activity of this type of catalysts in the transesterification reaction of low-grade feedstocks for biodiesel production. These catalysts show good catalytic performance during the biodiesel production from different feedstocks. The serious problem associated with the heterogeneous catalyst is its deactivation, which in turn reduce the catalyst reusability and chemical stability. These two factors play a key role in the biodiesel production cost, which is the main hurdle for its commercialization. In the view of the literature presented, it shows that the biodiesel technology is still not so mature to contribute more for overcoming the energy needs. Therefore, efforts are still in progress all over the world to develop an efficient bifunctional catalyst for biodiesel production

to overcome the serious disadvantages associated with the present biodiesel production technology. The bifunctional heterogeneous catalysts developed in the last few years are studied in detail below.

Yan et al. [64] synthesized novel zinc and lanthanum mixed oxides as heterogeneous catalysts for biodiesel production from unrefined or waste oils. They also studied the physico-chemical properties of the synthesized catalysts, effects of the metal oxide molar ratio, free fatty acids and water contents in feedstock, molar ratio of methanol and oil, and reaction temperature, on the yield of biodiesel. The authors found that a strong interaction between the Zn and La species existed with enhanced catalyst activities. Moreover, lanthanum enhanced the zinc oxide distribution, thereby, increased the surface acid and base sites which in turn enhanced the catalyst ability for simultaneous transesterification and esterification reactions. They reported that the catalyst with a 3:1 ratio of zinc to lanthanum could effectively catalyze both transesterification/esterification reactions, and with negligible hydrolysis activity in oil as well as in biodiesel. The biodiesel yield of 96% of fatty acid methyl esters (FAME) was recorded within 3 h using waste oils in reaction temperature range of 170–220°C.

Macario et al. [108] produced biodiesel from waste oilseed fruits with methanol in the presence of heterogeneous/homogeneous systems using acid and basic catalysts. The authors synthesized catalysts with strong acid sites (USY, BEA, FAU-X) and catalysts with weak acid sites (MCM-41 and ITQ-6) by the hydrothermal process. Potassium was introduced into different materials by ionic exchange such as K-MCM-41 and K-ITQ-6 to prepare bifunctional catalysts (acid–base catalysts). They found that highest triglyceride conversion and biodiesel yield values could be achieved using K-ITQ-6 catalysts in reaction time of 24 h at 180°C temperature. They further demonstrated that deactivation of the catalyst occurred due to potassium leaching. The catalyst exhibited good regeneration viability and could be reused for biodiesel production from low-quality oil for cheaper biodiesel production.

Cannilla et al. [109] investigated the catalytic performance of the MnCeO_x type bifunctional catalyst using refined sunflower oil for biodiesel production with methanol. They synthesized a series of manganese-ceria catalysts with the Mn/Ce atomic ratio ranging between 0.4 and 3.4 by the redox-precipitation method. NH_3 -TPD and CO_2 -TPD were utilized for acid-base active sites measurements on the surface of MnCeO_x catalysts. It was found that MnCeO_x catalytic systems exhibited high surface area, high chemical and thermal stability and high Mn dispersion, thereby resulted in high biodiesel production by the transesterification reaction of sunflower oil with methanol at a temperature of 140°C in 5 h of reaction time at low catalyst/oil ratio (1 wt.%). Moreover, the catalyst showed excellent catalytic stability and the deactivation phenomenon was found to be lower than that employed for acid catalytic reactions. They concluded that catalyst performance was the result of a synergic role played by both the surface acid/base character and textural porosity.

Wen et al. [110] prepared a TiO_2 –MgO bifunctional mixed oxide catalyst by the sol–gel method to carry out simultaneous transesterification and esterification reactions in waste cooking oil into biodiesel. They found that the catalyst with one molar ratio of Ti and calcined at 923 K

exhibited high activity and stability in the biodiesel reaction. They suggested that titanium improved the stability of the catalyst as a result of defects induced by the substitution of Ti ions for Mg ions in the magnesia lattice. Furthermore, they found that the MT-1-923 catalyst provided maximum biodiesel yield of 92.3% in the first use and increased after reuse of fourth time. The increase in the catalytic activity was attributed to increase in the specific surface area and average pore diameter after regeneration. The TiO_2 -MgO mixed oxide catalyst showed good potential in large-scale biodiesel production from waste cooking oil.

Borges et al. [111] studied biodiesel production from sunflower oil and frying oil with a bifunctional heterogeneous catalyst derived from natural porous silica, pumice. The bifunctional activity of the catalyst was enhanced by introduction of K into the catalyst. They further investigated the dependence of the reaction variables such as temperature, reaction time, catalyst loading, and methanol/oil molar ratio on biodiesel yield using sunflower oil and waste oil as feedstocks. The natural material, pumice exchanged with a KOH aqueous solution demonstrated to be an efficient bifunctional heterogeneous particulate catalyst for simultaneous transesterification of triglycerides and esterification of free fatty acids present in sunflower oil and waste frying oil at low temperature (55°C). Moreover, the reusability studies showed that there was no considerable change in the activity of the catalyst even after five regenerations, demonstrating it to be a stable material.

Misra et al. [112] synthesized bifunctional heterogeneous catalysts by the conventional sol gel method for biodiesel production from different feedstocks such as soy, canola, coffee and waste vegetable oils containing variable amounts of free fatty acids (0–30 wt%). The authors reported that the synthesized bifunctional Quntinite-3T catalyst could effectively converted the free fatty acids and triglycerides (TGs) simultaneously into biodiesel in a single step of batch reactor. Similarly, Quntinite-3T also showed substantial reusability up to five times with more than 95% catalytic activity.

Omar et al. [107] studied the catalytic activity of alkaline modified zirconia (Mg/ZrO_2 , Ca/ZrO_2 , Sr/ZrO_2 , and Ba/ZrO_2) to identify an efficient bifunctional heterogeneous catalyst for biodiesel production from waste cooking oil (WCO). Physicochemical properties of the synthesized catalysts were analyzed by BET surface area, XRD, FESEM and CO_2 - NH_3 -TPD. The authors reported that among different synthesized catalysts, Sr/ZrO_2 exhibited higher catalytic activity due to the presence of optimal active basic/acidic sites, facilitating simultaneous transesterification and esterification reactions in WCO. The results demonstrated that the methyl ester (ME) yield of 79.7% could be obtained by using 2.7 wt% catalyst loading (Sr/ZrO_2), 29:1 methanol to oil molar ratio, 169 min of reaction time and 115.5°C temperature.

Jiménez-López et al. [113] reported that incorporation of the WO_x species into a mesoporous zirconium-doped silica could lead to an effective catalyst formulation that could catalyze both transesterification and esterification reactions in the used oil. During their investigations, they found that the catalyst calcined at 700°C with 15 wt% WO_3 loading provided the biodiesel yield higher than 80% after 2.5 h reaction time at reaction temperature of 200°C in the presence of methanol. Moreover, the catalytic activity could be main-

tained even in the presence of 5 wt% of water and after three cycles of re-utilization, without any further treatment of the catalyst.

Salinas et al. [114] investigated the catalytic performance of potassium supported on titania as a catalyst for the production of biodiesel from canola oil. The authors reported that low loadings of potassium lead to the formation of weak basic sites on the acid support (titania), therefore exhibited bifunctional behavior to produce biodiesel from low cost feedstocks. Furthermore, they added that the synthesized catalyst presented interesting activities with robust character since there was no need for in situ pre-treatment or inert reaction environment.

Farooq et al. [115] employed mixed oxide supported bifunctional heterogeneous catalysts in biodiesel production from waste cooking oil. The author reported that the synthesized catalysts show improved transesterification activities and provided the maximum biodiesel yield of 91.4% in reaction time of 4 h at a reaction temperature of 100°C, methanol to oil molar ratio of 27:1 and an agitation speed of 500 rpm. Moreover, the synthesized catalyst showed substantial chemical stability and could be reused for at least eight times without major loss in its catalytic activity. The catalyst deactivation in the higher run was attributed to strongly adsorbed organic molecules onto the active sites and leaching of the various active metals during biodiesel production from waste cooking oil. They further concluded that the physicochemical properties of the biodiesel produced from waste cooking oil comply with the international standard specifications.

Similarly, Taufiq and his research team [116] modified La_2O_3 with Bi_2O_3 (1–7 wt%) to develop an efficient catalyst for simultaneous esterification and transesterification reactions at atmospheric pressure. The catalysts were characterized by X-ray diffraction (XRD), BET surface area, desorption of CO_2 (TPD- CO_2) and NH_3 (TPD- NH_3). The authors found that the bismuth concentration significantly affected the performance of the catalyst and La_2O_3 - Bi_2O_3 mixed with 5 wt% bismuth exhibited excellent transesterification activity for biodiesel production from jatropha oil. The bifunctional catalyst, under optimal reaction condition of methanol/oil molar ratio of 15:1, 2 wt% of the catalyst amount, reaction temperature of 150°C and reaction time of 4 h, provided the highest conversion of 93% from jatropha oil. This catalyst maintained 87% of FAME conversion after three successive recycling experiments. The decrease in the catalytic activity of the La_2O_3 - Bi_2O_3 catalyst was related to the decrease in the concentration of Bi and La metals in the catalyst when used in transesterification of jatropha oil.

Taufiq [28] and his research group also reported a CaO - La_2O_3 mixed oxide based bifunctional heterogeneous catalyst for biodiesel production from jatropha oil. They studied the stability of the CaO - La_2O_3 binary system in detail for the sustainable biodiesel process. The authors mentioned that the metal-metal oxide network between Ca and La resulted in well dispersion of CaO on the composite surface and thereby, increased the number of active acidic and basic sites as compared to that of bulk CaO and La_2O_3 metal oxide which in turns enhanced the catalytic activity. Furthermore, the biodiesel conversion increased with the increase in the Ca/La atomic ratio up to 8.0, where the stability of the CaO - La_2O_3 binary system decreased at the Ca/La atomic ratio of 10.0 due to highly saturation of CaO on the catalyst surface. The authors reported highest biodiesel yield of 98.76% at 160°C, 3 h, 25 methanol/oil molar ratio and 3 wt

%. In addition, the $\text{CaO-La}_2\text{O}_3$ binary system was stable even after four cycles with negligible leaching of Ca^{2+} ion into the reaction medium.

Alhassan et al. [117] reported $\text{Fe}_2\text{O}_3\text{-MnO-SO}_4^{2-}/\text{ZrO}_2$ nano sized bifunctional heterogeneous catalysts for biodiesel production from low-grade waste cooking oil. The physicochemical properties of the synthesized catalysts were studied by using X-ray diffraction (XRD), Temperature Programmed Desorption of NH_3 (TPD- NH_3/CO_2), Thermal gravimetric analysis (TGA), Fourier Transform Infrared Spectroscopy (FT-IR), Brunner–Emmett–Teller (BET) surface area measurement, Energy Dispersive X-ray Spectroscopy (EDS), Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). The authors reported that the catalyst could be reused six times without any substantial loss in its catalytic activity with the maximum yield of $96.5 \pm 0.02\%$ at the optimized conditions of the reaction temperature of 180°C ; stirring speed of 600 rpm, 1:20 M ratio of oil to alcohol and 3 wt/wt% catalyst loading.

Recently, zinc oxide (ZnO) nanostar, synthesized by the microwave-assisted surfactant free hydrolysis method was applied as the catalyst for biodiesel synthesis through one-step simultaneous esterification and transesterification from high free fatty acid by Kwong et al. [118]. The author reported that the ZnO nanostar catalyst showed high stability and robustness at the end of the reaction, providing a biodiesel yield of 97.3% via simultaneous esterification and transesterification in low grade feedstock like waste cooking oil and crude plant oils. They pointed out that the high efficiency of the synthesized catalyst could be attributed to the in-situ formation of the ZnOl intermediate and the ZnGly deposited on the catalyst surface to form a new co-catalyst.

In the view of above discussion, bifunctional heterogeneous catalysts seem to be a promising technology for biodiesel production from low-grade feedstocks, but after several time usage their catalytic activity topple down due to deactivation by strong adsorption of organics and leaching of the various active metals during transesterification of low-cost feedstocks. Hence, still there is enough gap for improvement to develop a robust bifunctional heterogeneous catalyst and incorporate desired physicochemical properties with enhanced catalytic activity, selectivity, and stability for economical biodiesel production from low cost feedstocks.

5. Recommendation

Environmentally friendly and efficient heterogeneous catalysts for a sustainable biodiesel technology are getting more and more attention among the research communities. The invention of the novel heterogeneous catalysts that have desirable physical and chemical properties, more stable, durable, and efficient under ambient conditions is one of the primary goals in focus of many research communities. The following steps may be recommended to design an efficient catalyst for sustainable biodiesel production from different biomass.

1. An appropriate catalytic configuration and preparation method may be adopted to design an efficient bifunctional catalyst with desired physical and chemical properties, which in terms help to achieve good thermal and mechanical stability.

2. The catalyst structure-activity correlation should be thoroughly defined by evaluating the physicochemical properties of the synthesized catalyst using different analytical techniques to develop a robust bifunctional heterogeneous catalyst with desired physicochemical properties to carry simultaneous esterification and transesterification reactions in the low-grade feedstocks. The physicochemical properties of the bifunctional heterogeneous catalyst may be tuned to get optimum number of active sites, which in terms would improve the catalytic activity, stability during biodiesel reaction from low grade feedstocks for sustainable energy process.
3. The use of waste materials such as animal bones, naturally available clays, etc., should be utilized as raw materials for catalyst preparation. The use of raw materials in the biodiesel technology will further contribute to low-cost biodiesel production. These materials may be modified to develop an effective catalyst which may be used several times for biodiesel production from low cost feedstocks.

Currently, our research group is also working on the modification of naturally available clay for biodiesel production from waste cooking oil. We have introduced different metals and groups into selected clays by the modified impregnation method to develop bifunctional activity of the catalyst with enhanced catalyst stability and activity for sustainable biodiesel technology.

6. Conclusion

The use of bifunctional heterogeneous catalysts for biodiesel production seems to be a promising technology for the efficient biodiesel production from low cost feedstocks, such as waste cooking oil for sustainable energy production. Therefore, it is essential to design a bifunctional heterogeneous catalyst with desired physical and chemical properties, which show potential ability to carry simultaneous esterification and transesterification reactions in low grade feedstocks for sustainable biodiesel production. The catalyst structure-activity correlation should be properly studied to modify the physicochemical properties of the synthesized catalyst to design an effective heterogeneous catalyst for biodiesel production. Moreover, the use of waste cooking oils as feedstocks and waste materials for catalyst preparation is very interesting, and may further make the biodiesel production process economically feasible and will greatly decrease the production cost of biodiesel.

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