A Review on Application of Heterogeneous Catalyst in the Production of Biodiesel from Vegetable Oils

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Abstract

Biodiesel has been considered as one of the interesting alternative and environmentally benign fuels. The development of environmental friendly heterogeneous catalyst for the esterification/transesterification process seems to be promising route and the reason why it is more preferred to conventional homogeneous and enzymatic catalyzed reactions is discussed. However, investigation on heterogeneous catalyst for biodiesel production is extensively carried out based on previous research studies. In order to reduce cost of biodiesel production, evaluation and characterization of heterogeneous catalytic materials before and after its preparation provide facts on the process that have significant impact on the desired activity and selectivity properties. This review study provides a comprehensive overview of common process techniques usually employ in producing biodiesel. Different materials that serve as sources of heterogeneous catalysts to transesterify oils or fats for production of biodiesel with emphasis on selection criteria of solid catalytic materials are also highlighted. The potential heterogeneous catalyst that could be derived from anthill, various methods of preparing solid catalysts, as well as reusability and leaching analysis are discussed in details.

Keywords: *Biodiesel, Heterogeneous catalyst, Leaching, Transesterification, Vegetable oils*.

1. Introduction

Biodiesel is cleaner burning fuel similar to fossil diesel in terms of qualities and features. However, because of biodiesel uniqueness, it seems to be higher in quality than conventional fossil diesel [1], the comparison between fossil diesel and biodiesel by considering their physicochemical properties are presented in Table 1. With few years of its discovery and commercial use, biodiesel through its properties, has proven to be suitable for powering diesel engines [2]. It is obtained from renewable resources, sustainable and also lowers the life cycle of greenhouse gases by significant amount compared to fossil diesel [3]. Moreover, in most of the developed countries, regulations have restrained sulphur content in diesel fuel within the acceptable limit of 50 ppm. It was observed that sulphur provides fossil diesel with lubricity that will vanish as the regulations fully take effect [3]. However, blending of appropriate amount of biodiesel with fossil diesel has a significant impact in restoring lubricity via an anti-wear on injection system of engine [4-5]. Thus, there is urgent need to

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source for alternate fuel, which is sulphur content free, non-poisonous, renewable and biodegradable [6], this becomes imperative due to the fact that, the depletion of petroleum-based fuel has increased the price of diesel extraordinarily and also, greenhouse gas emission is of environmental concern [7].

Table 1: Comparison between physicochemical properties of petrol-diesel and biodiesel based on ASTM standard

Property	Unit	Fossil diesel	Biodiesel
Standard	-	ASTM D975	ASTM D6751
Composition	-	Hydrocarbon (C_{10}-C_{21})	Fatty acid methyl ester (C_{12}-C_{22})
Specific gravity	-	0.85	0.88
Flash point	K	333-353	373-443
Cloud point	K	258-278	270-285
Pour point	K	243-258	258-289
Carbon content	wt.%	87	77
Water content	vol.%	0.05	0.05
Cetane number	-	40-55	48-60
Sulphur	wt.%	0.05	0.05
Hydrogen	wt.%	13	12
Oxygen	wt.%	-	11

Source: [1]

In most countries, standard specifications for biodiesel has been put in place, for instance, ASTM D6751 and EN 14212 are being used in America and Europe respectively as biodiesel standard specifications, because European biodiesel standard is somehow stricter than American standard, EN 14212 is now being used by most countries [8]. In general, a code comprising a number indicating the content of biodiesel in percentage is used; for instance, B100 comprises of 100% biodiesel (uncontaminated biodiesel) while B20 is made up of 20% biodiesel and 80% petroleum diesel. In Sweden, B5 is frequently used as vehicular fuel, but according to EN 590:2009 diesel standard, B7 is the highest biodiesel blend for utilization in diesel engines [9] [BS EN, 2009]. Recently in Nigeria, the Nigerian National Petroleum Corporation (NNPC) had decided to improve the quality of diesel being produced in the country by blending 80% fossil diesel with 20% biodiesel and this would go a long way in reducing the greenhouse gas emission [10]. This present study provides an overview of the application of heterogeneous catalyst in the field of renewable energy with special emphasis on its development from different sources to facilitate the synthesis of biodiesel from both edible and non-edible oils. Different methods of producing biodiesel, various catalyst preparation methods, as well as catalyst reusability and leaching analysis are discussed and highlighted.

2. Biodiesel production

There are five major techniques used for lowering the viscosity of vegetable oils for practical use in existing engines. These methods are pyrolysis, microemulsification, blending, transesterification or esterification and supercritical process. Although, bleeding and microemulsification are not production processes. Blending is achieved through physical mixing of vegetable oil with fossil diesel while microemulsification is colloidal equilibrium dispersion spontaneously from two immiscible fluids. Lower viscosity is achievable through these methods. However, similar engine performance is still encountered using these two techniques [11].

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Pyrolysis or thermal cracking is the breaking down of organic matter in the absence of air. In this case, heat and catalyst are involved in thermal cracking of vegetable oils or fat into smaller components at temperature ranging between 400 and 450 ^{o}C [12]. Diesel–like fuel is thus obtained with similar properties to fossil diesel [13]. The diesel fuel derived from pyrolysis of vegetable oil or animal fat contains mostly olefins, paraffin, and esters. Unlike blending and microemulsification techniques, diesel fuel derived from pyrolysis process is clean and does not suffer engine performance issues; it is energy consuming and needs expensive separation unit [14]. More so, the sulphur and ash contents make pyrolysis technique less environmental friendly [15].

In the past, blending, microemulsification and pyrolysis techniques have been successfully employed for diesel oil production from vegetable oil or fat, today, transesterification process is a commonly used method for the biodiesel production [16]. In general, transesterification is the direct conversion of one ester to another through interchange of special functional group called alkoxy moiety [17]. In this method of biodiesel production, the triglycerides present in vegetable oil or fat react with monohydric alcohol (methanol, ethanol, and butanol) in the presence of a catalyst. Biodiesel production via transesterification necessarily requires a catalyst to attain the equilibrium in practical manner [18]. The required catalyst can either be homogeneous or heterogeneous or enzyme. In the transesterification process, three consecutive reactions are required as illustrated in Equations 1- 4. The first reaction is the one between triglyceride (TG) molecules present in oil and excess methanol (A) usually methanol which gives di-glyceride (DG) (intermediate) and methyl ester (ME). The di-glyceride (DG) then reacts with part of the remaining methanol leading to the formation of another intermediate (mono-glyceride [MG]) and more methyl ester (ME). The intermediate formed in the second reaction then also combines with remaining methanol to give more methyl ester (ME) and glycerol (G). Occasionally the mono-glyceride (MG) (intermediate) is destroyed in the last reaction step.

$$TG + CH_3OH(A) \xleftrightarrow{catalyst} DG + ME \quad (1)$$

$$DG + CH_3OH(A) \xleftrightarrow{catalyst} MG + ME \quad (2)$$

$$MG + CH_3OH(A) \xleftrightarrow{catalyst} G + ME \quad (3)$$

$$TG + 3CH_3OH(A) \xleftrightarrow{catalyst} G + 3ME \quad (4)\ \text{(Overall reaction)}$$

(a) Equations (1) - (3) are transesterification reaction steps (b) Equation (4) is the overall transesterification with methanol.

Meanwhile, there is another advanced form of traneseterification process called non-catalytic supercritical transesterification. This method does not require catalyst to speed up the reaction rate [19]. Non-catalytic supercritical transesterification is usually carried out in a homogeneous phase by subjecting solvents such as water, methanol, ethanol, propanol, as well as butanol to high temperatures and pressures in order to make them act as super acids [14]. Under supercritical conditions, alcohol performs the roles of catalyst and reactant [20]. Saka and Kusdiana [19] had investigated a non-catalytic biodiesel production process by using supercritical method. A conversion of rapeseed oil of 98.5% was achieved under favourable supercritical conditions of 350 ^{o}C temperature of reaction, 43 mPa pressure, 240 s reaction time and 42:1 molar ratio of methanol to oil. In spite of high product yield and purity, the high cost of production makes this technique not viable for commercial production [21]. The use of co-solvent and supercritical CO_2, as a reaction medium in the presence of catalyst to allow the supercritical reaction to take place under moderate conditions has been proposed [22]. Using supercritical carbon dioxide as a reaction medium has proven to be an efficient alternate to operate at moderate conditions [23]. Alves *et al*. [23] synthesized fatty acid methyl esters (FAME)

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from used frying oil by transesterification with ethanol and methanol using supercritical carbon dioxide, as a reaction medium in the presence of zinc aluminate as heterogeneous catalyst. The optimization of reaction parameters carried out showed that optimum yield of biodiesel could be obtained at 200 ^{o}C after 30 mins of reaction under alcohol: oil molar ratio of 40:1 and 700 rpm stirring [23].

2.1 Catalysts in transesterification reaction

Biodiesel production necessarily requires a catalyst to attain the equilibrium in a practical manner [18]. Required catalyst can either be homogenous or heterogeneous. Acid based homogeneous catalyst such as H_2SO_4 and HCl, and alkaline- based homogeneous such as KOH and NaOH, cater to the present need for biodiesel synthesis [24]. However, there are problem associated with these homogeneous catalysts. Acid-based homogeneous catalysts operate at high temperature, difficult to recycle, corrosive in nature and also take more time to attain equilibrium state during biodiesel synthesis [25-26]. Although, alkaline-based catalysts take less time, it reacts with free fatty acid (FFA) to form undesirable product (soap) which in turn increases pH of the fatty acid methyl esters [27] and thus requires expensive separation[18, 28-30]. Nowadays, many authors centered their researches on how suitable catalyst that can be easily separated from reaction mixture, reused and provided maximum conversion without creating any downstream problems, could be formulated [25-26, 31].

In contrast, heterogeneous catalysts can lower the cost of production and also make its sustainable. This is because when catalyst is not in the same phase with reactants/products, product separation is quite easy and catalyst recovery is also realistic. In heterogeneous catalysis, high pressures and high temperatures are required in transesterification for higher yield of biodiesel. This depends on the form of catalyst employed and preparation method adopted [32]. However, the physical and structural properties of catalyst need to be adequately formulated during catalyst preparation to obtain good results. Different varieties of solid catalysts for converting oil or fat into biodiesel have been extensively investigated and documented in the literature. Most of these heterogeneous catalysts include pure metal (alkaline earth, transition) oxides, mixed-metal oxides and supported metal oxides [17]. More so, biomass derived heterogeneous catalysts have been widely studied and reported for biodiesel production [25]. However, heterogeneous catalyst is sensitive to free fatty acid (FFA) content in feedstock and if FFA content in the oil exceeds 2 wt%, it leads to soap formation, besides, if heterogeneous catalyst is not anchored by a support, the active ingredient leaches into reaction medium, thus leading to product contamination [33].

Utilization of biocatalyst for the transesterification of vegetable oil is continuously attracting much attention and the enzymes perform excellently and equal well with homogeneous and heterogeneous catalysts [34]. Pazouki *et al.* [35] investigated the activity of immobilized cell of *Rhizopus oryzae* in biomass support particles (BSPs) during waste cooking oil conversion. However, 88% methyl esters conversion was achieved. Abdulla and Ravindra [36] immobilized lipase from *Burkholderia cepacia* to catalyze the transesterification of crude J.curcas L. oil to achieve 73% methyl ester conversion and the immobilized lipase remained stable after six successive cycles of reuse. Ragauskas *et al.* [37] made use of *Rhizopus oryzae* as biocatalyst in the conversion of three different oils under the favourable reaction conditions. However, as widely reported in the literature, enzymatic transesterification reaction needs to be carried out at moderate condition so as to prevent enzyme deactivation [38], besides, enzyme-catalyzed transesterification is not cost effective, because enzymes are costly and require a prolong period of reaction [34].

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3. Biodiesel production via heterogeneous catalytic process

In spite of the meaningful progress in biodiesel production technology, its commercialization still relies on the availability of suitable catalysts; this has a direct impact on the amount of catalysts required during transeterification reaction. The factors include the periodic replacement of catalysts, desired promoter and oil conversion to achieve optimum yield, catalyst stability, as well as the overall performance of continuous heterogeneous catalyzed systems. Therefore, the desired characteristics of a suitable heterogeneous catalyst [39] are selectivity, purity, high activity, regenerability, simple and low manufacturing cost, less environmental impact. Research had shown that these key catalyst characteristics could be easily attained with mono-metal oxides (pure metal oxides) [40]. Kinetic studies of sunflower conversion over CaO catalyst was carried out by Vujicic *et al.* [41]. It was observed that CaO as a mono-metal oxide heterogeneous catalyst is capable of esterifying vegetable oil.

The activities of thirteen different kinds of pure alkaline earth metal oxides were investigated in the transesterification of soybean oil at reaction temperature of 60 ^{o}C and methanol to soybean oil ratio of 6:1 for 10 h [42]. However, the oxides consist of calcium showed good catalytic performance and 90% methyl ether yield was obtained [42]. From previous studies [17, 43], owing to its high availability, slight solubility in methanol, high basic strength, minimum environmental impact, non-poisonous, calcium oxide (CaO) has been extensively used as catalyst for biodiesel production.

3.1 Mixed-metal oxide and sulphated-metal oxide catalyst

The use of mixed-metal oxides or their complexes as heterogeneous catalysts had shown good activity for biodiesel production compared to their mono-metal oxides counterpart. The use of support or promoter on active site of a catalyst has been identified as a helpful option for reducing the quantity of catalyst needed and achieve the same degree of conversion and level of catalytic activity [17]. Recent researches carried out had proven that mixed/sulphated metal oxides have very good physical and structural properties as compared to monometallic oxides [44]. Therefore, several investigations were centered on the preparation from local and low cost materials, characterization and evaluation of its performance during first and subsequent cycles.

Table 2 summarized various mixed and sulphated metal oxides employed as heterogeneous catalysts for biodiesel production. Mixed CaO-MgO had been reported as the most promising catalyst examined [45]. The authors observed that the addition of MgO on CaO and ZnO enhance their activities, but causes formation of soap in the reaction process. Sirichai *et al*. [46] prepared CaO-ZnO catalyst by two different methods for the conversion of palm oil. The two catalysts gave high yield of biodiesel under favourable reaction conditions.

Other than the use of mixed metal oxide for biodiesel synthesis, more complex metal oxide mixed with sulphated materials had been investigated to be applied as heterogeneous catalyst in the conversion of vegetable oils [56, 57, 61]. Lam and Lee [59] investigated the transesterification of waste cooking with mixed methanol-ethanol over SO_4^{2-}/SnO_2-SiO_2 catalyst and FAME yield of 81.4% was obtained at optimum reaction conditions. This novel approach reduces the limitation of using ethanol in a heterogeneous acid catalyzed transesterification process and also improves the quality of the prepared biodiesel. More so, Kafuku *et al.* [58] reported biodiesel synthesis from moringa oleifera oil using $SO_4^{2-}/SnO_2/SiO_2$ catalyst. The effects of varying reaction parameters were studied and the yield up to 84% of biodiesel was obtained at optimum reaction conditions [58]. Furthermore, sulphated zirconia alumina catalyst ($SO_4^{2-}/ZrO_2/Al_2O_3$) had proven to be effective in the transesterification of palm oil with methanol. However, an optimum palm oil conversion of 83.3% was achieved at favorable conditions [62].

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Table 2: Summary of mixed metal oxides and sulphated-metal oxide catalyst used for biodiesel production

Mixed / Sulphated Metal Oxide	Feed stock	Biodiesel Yield (%)	Reference
CaO-ZnO	Palm oil	79.6	[46]
Al_2O_3-ZrO_2	Soybean oil	80	[47]
CaO-Al_2O_3	Microalga's lipid	97.5	[48]
WO_3-ZrO_2	WCO	96	[49]
La_2O_3-ZrO_2	Sunflower oil	94	[50]
TiO-MgO	CTS oil	-	[28]
CaO-CeO_2	Rapeseed oil	>80	[42]
ZrO_2-WO_3	Palmitic acid	98	[51]
CaO-ZnO	PKO	-	[52]
ZnO-La_2O_3	Waste oil	-	[53]
ZrO_2/WO_3/Al_2O_3	Soybean oil	94	[54]
MgO-ZnO	Free fatty acid	89.3	[55]
SO_4^{2-}/ZrO_2	Palm kernel oil	90.3	[56]
SO_4^{2-}/ZrO_2	Coconut oil	86.3	[56]
SO_4^{2-}/TiO_2-SiO_2	Cotton seed oil	92	[57]
SO_4^{2-}/SnO_2-SiO_2	Moringa Oleifera oil	84	[58]
SO_4^{2-}/ SnO_2-SiO_2	WCO	81.4	[59]
SO_4^{2-}/ZrO_2	Free fatty Acid	>25	[60]

3.2 Natural and low cost materials as heterogeneous catalysts

There is an increasing interest in searching for naturally occurring minerals and domestic waste materials as heterogeneous catalysts due to their low cost and availability in abundance. Most of these materials have been reported to be promising options in synthesizing biodiesel via heterogeneous transesterification. As these materials provided a clean, almost glycerol free biodiesel and also reduce biodiesel production cost. Waste food materials have been largely analyzed as potential sources of calcium oxide catalyst [63] and are mainly comprised of calcium compound, which decompose to calcium oxide (CaO) when it is subjected to calcination process. Calcium oxide (CaO) is the active phase that behaves as heterogeneous catalyst. Waste materials such as shrimp, oyster, crab, snail, cockle, chicken egg shell, as well as, fish bone, animal bone and cuttle bone had been identified as natural waste sources to synthesis calcium oxide [18, 63-64] as illustrated in Table 3.

Sulaiman *et al.* [63] studied the use of fish bone as catalyst for biodiesel production. However, the X-ray diffraction and scanning electron microscope analyses carried out on calcined fish bone showed that it contains calcium oxide, calcium phosphate and hydroxyapatite. Shah *et al.* [65] had recorded success in using crab shell, eggshell and fish bone as heterogeneous catalyst to produce biodiesel. These waste food materials were calcined individually to obtain calcium oxide (CaO). Transesterification was then carried out with calcined CaO obtained from each of those materials at 65 ^{o}C for 4 h with varied methanol to oil ratio. It was found that each catalyst produced different biodiesel yields depending on their calcination period, fish bone, eggshell and crab provided yield of 77.2%, 65% and 62% respectively. Fish bone provided outstanding results among the three catalysts, followed by eggshell [65].

More so, waste fish scale had been used as heterogeneous catalyst to transesterify soybean oil with methanol at varying catalyst concentration of 1-5 wt% for 5 h. The reaction which was carried

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out at temperature of 70 ^{o}C yielded 97.73% of biodiesel [66]. Furthermore, waste chicken eggshell [67], waste shells of mollusk [68], Oyster shell [69] and waste fish and other animal bones [63] had been used for biodiesel production and greater than 80% yield of biodiesel was recorded.

Recently, interest in the application of clay as catalytic material in renewable fuel production has been shown by several researchers due to the availability of this natural material with strong chemical activity [31, 70-71]. Olutoye and Hameed [31] investigated the catalytic activity of clay for transesterification reaction. The clay sample which was thermally treated at calcination temperature of 830 ^{o}C for 4 h showed better performance amongst various as-synthesized clay catalysts by providing biodiesel yield of 96% at optimum reaction temperature, time, methanol to oil ratio and catalyst loading of 150 ^{o}C, 5 h, 15:1 and 3.5 wt%, respectively. The result obtained by these authors indicates that the application of clay as solid catalyst in biodiesel production could avoid the use of expensive rare earth metals and thus, solve the leading problem associated with these metals [31].

Table 3: Summary of operation conditions for different naturally occurring and waste materials used as heterogeneous catalysts

Source of catalyst	**Biodiesel feedstock**	**Preparation condition**	**Biodiesel yield (%)**	**Reference**
Clay	Waste cooking palm oil	Calcination at 830 ^{o}C for 4 hr	96	[31]
Barium – modified montmorillonite (BMK10)	Waste cooking oil	Impregnation + calcination at 500 ^{o}C for 5 h	88.38	[72]
Modified – peanut husk ash	Soybean oil	Heating of husk at 900 ^{o}C for 2 h + mixing with Li_2CO_3 + calcination for 4 h	98.4%	[73]
Chicken eggshell	Soybean oil	Calcination at 1000^{o}C for 2 h	95%	[74]
Fish bone	Palm oil	Calcination at 900 ^{o}C for 2 hr	77.2	[65]
Waste animal bone	Palm oil	Calcination	96.78	[64]
Snail shell	Waste frying oil	Calcination at 900 ^{o}C for 3.5 hr	87.28	[68]
Shrimp shell	Rapeseed	Carbonization + impregnation + calcination for 2 hr	89.1	[75]
Chicken eggshell	Pongamia pinnata	Calcination at 900 ^{o}C for 2 hr	95	[18]
Ostrich eggshell	Waste cooking oil	Calcination at 1000 ^{o}C for 4 hr	96	[67]
Quail eggshell	Palm oil	Calcination at 800 ^{o}C	98	[76]

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3.3 Potential heterogeneous catalyst from anthill

Anthill is a naturally occurring material which can serve as potential catalyst in transesterification process. As shown in Table 4, anthill sample contains several metal oxides in which some of them in their pure forms have been used as catalysts for biodiesel synthesis [41, 69]. An anthill is a form of siliceous or fire clay which is formed at the entrances of subterranean dwelling of ant colonies [77-78]. An ant colony is an underground chamber where ants live and is being built and maintained by worker ants. According to Paton *et al*. [79], anthill is classified into two categories, namely type I and type II anthills. Type I nest is less noticeable in the ant territory, because it is small in size and shape. However, they are characterized by waste deposition and are easily influenced by erosion [80-81]. By comparison, types II mound as shown in Figure 1, is huge, often stick together, sometimes surrounded by vegetation and persist for many years [78].

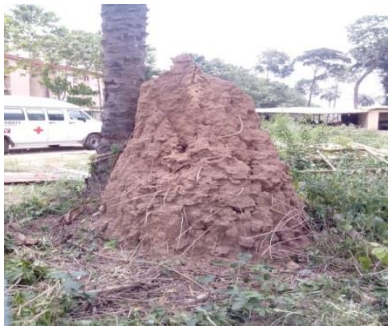

Figure 1: Type II anthill located in Afe Babalola University, Ado Ekiti Nigeria on an elevation of 1165 ft above sea level, having latitude (N7^{o}36.409$^{/}$) and longitude (E005^{o}18.627$^{/}$).

Research has proven that anthill contains a high percentage of silica. Henne [78] carried out chemical analysis on samples of anthill soil from different locations. The result obtained showed that all the samples have large silica content, followed by alumina and it was also noticed that chemical compositions of those components contained in anthill samples from different locations vary. Table 4 shows chemical composition of two different anthills from two different locations in west Africa.

Table 4: Compositional analysis of anthill from two different locations

Constituent	**Anthill chemical composition (%)**	
	Biadan Ghana Anthill	Akure Nigeria Anthill
SiO_2	68.70	58.83
Al_2O_3	18.43	22.69
Fe_2O_3	2.36	2.42
MgO	0.44	0.84
CaO	0.41	0.01
Na_2O	0.20	0.06
K_2O	1.60	2.10
TiO_2	1.30	0.72
Others	5.56	12.33

Source: [78, 82]

Anthill materials are important constituents of landscape not only because they are readily available but mainly because of their industrial usefulness. For example, it has been used to make

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ceramic and furnace [78], cement, bricks and sand casting [83] and refractories [82]. More so, due to the presence of silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3) and calcium oxide (CaO), anthill has potential ability to be employed as industrial heterogeneous catalyst. Besides, it is readily available and environmentally benign. However, potential application of anthill as catalyst for biodiesel production is attributed to the presence of CaO, Al_2O_3 and SiO_2, which can serve as active ingredient, promoter and support respectively. Although research and experimental studies on clay and its composites had been conducted[31, 72, 84], as reflected in literature, anthill (a form of clay) has not been used as catalyst for the transesterification reaction. Since anthill belongs to a class of clay and contains silica as the major component it can be used to make supported/composite catalyst by impregnating it with another active ingredient such as waste chicken eggshell. Therefore, research on the development of composite anthill-chicken eggshell as heterogneous catalsyt for biodiesel production from waste frying oil is on going by the respective authors.

3.4 Preparation of the heterogeneous catalyst

Different methods used in preparing heterogeneous catalysts had been described and reported in the literature. Those methods include precipitation, impregnation, sol-gel and hydrothermal methods and are discussed as follows:

3.4.1 Precipitation method

With this method, solid catalyst which possesses high porosity could be synthesized. It involves the addition of a precipitating agent to solution of catalyst's precursor, followed by washing, drying, and calcination or activation [85]. Ngamcharussrivichai *et al*. [52] prepared by co-precipitation of Ca and Zn compounds with Na_2CO_3 as precipitating agent. Sirichai *et al*. [46] also synthesized CaO-ZnO catalyst via co-precipitation method and used it to speed up the rate of transesterification reaction between palm oil and methanol. Precipitation method was employed to prepare CaO-ZrO_2 catalyst with ammonia solution as precipitating agent [86]. More so, Macedo *et al.* [87] had made use of co-precipitation technique to prepare mixed oxides of aluminum, tin and zinc using sodium carbonate (IV) solution as precipitate. Furuta and his co-authors had investigated the use of precipitant to prepare $Al_2O_3/ZrO_2/WO_3$ catalyst, which was later employed to methanolize soybean oil [54].

3.4.2 Impregnation method

This method is an easy and simple method for preparing supported catalyst. It is done by bringing the solution containing catalyst's precursors in contact with porous supporting particles [88]. The excess solution is removed by draining and then heated at an elevated temperature to decompose the catalytic compound into metal oxide. Metal oxide reduction to metal is carried out by passing hydrogen gas through the reactor that contains metal oxide particles. The metal formed is activated to prevent contamination with air which might poison the reactive metal.

A lot of researchers had employed impregnation method to synthesize solid catalyst for the purpose of biodiesel production [89-91]. Taufiq-Yap *et al.* [92] impregnated sodium hydroxide on alumina ($NaOH/Al_2O_3$), followed by drying in an oven and also calcined for 3 h. The biochar-supported CaO (BCh-CaO) catalyst had been prepared by the wet impregnation method. Typically, a dried and powdered support was added to Ca- containing solution. The resultant mixture was stirred for few hours and later calcinated at a temperature of 600 ^oC under atmospheric pressure [93]. Abdoulmoumine [60] produced acidic solid catalyst by impregnation of Zirconium oxide with

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sulphuric acid for palmitic acid esterification. The synthesized catalyst (SO_4/ZrO_2) was able to be reused for various subsequent runs, indicating better stability. In the same vein, another impregnate (ZrO_2/NaOH) was also synthesized. It was calcined at a temperature of 600 ^oC and used for the conversion of soybean into Biodiesel [60].

Furthermore, Rutto [7] investigated the use of waste cooking oil for biodiesel production over thermally modified kaolin impregnated with potassium hydroxide. The catalyst was prepared at different mass ratio ranging between 1:2-1:6 and also calcined at temperature of 400 ^oC for 5 h. The optimum yield of biodiesel was found to be 95.06%.

3.4.3 Sol-gel method

Sol-gel is a special case of precipitation method, which is employed when the catalytic materials are colloidal in nature. Catalyst containing SiO_2 and alumina are usually prepared by gel formation [85]. Heydarzadeh *et al.* [94] had employed sol-gel method to coat clay plates against γ-Al_2O_3/ZrO_2 catalysts to esterify free fatty acid (FFA) with ethanol in a heterogeneous catalytic reaction. In this catalytic reaction, effects of some reaction variables were investigated. The obtained data proved that at optimum conditions, the FFA conversion to ethyl ester was 90%.

3.4.4 Hydrothermal method

A series of trimetallic composite nanoparticles were synthesized by doping $Pd_1NiAl_{0.5}$ onto multi-walled carbon nanotubes (MWCNTs) using a hydrothermal process. The amounts of PdO, $NiCl_2.4H_2O$ and Al_2O_3 were weighed according to the atomic ratio of Pd:Ni:Al. Three different samples with the atomic ratios of Pb:Ni:Al amounting to 1:2:0.5; 1:4:0.5 and 1:6:0.5, respectively, which were denoted as samples a, b and c. Another sample of Pd_1Ni_4/MWCNTs was synthesized using the same method without Al_2O_3, which was denoted as sample o. However, the results obtained from XRD analysis indicated that the active components of the resulting samples were PdO and metallic Pd. Also, the results of SEM and TEM analyses demonstrated that the atomic ratio of metals in the precursors played a key role in affecting the morphology and particle size of the catalyst [95]. This fact was also corroborated by Sue *et al.* [96]. The authors concluded that optimization of catalyst preparation conditions has significant effect on catalyst morphology and structure.

Furthermore, Man [55] in his work studied the performance of mesoporous Zn/MgO catalyst prepared by simple alkaline hydrothermal method. The catalyst was thermally treated at 600 ^oC and gave 88.7% biodiesel yield under the optimum reaction conditions. Besides, the catalyst proved to be stable as it was able to retain its activity over five consecutive experimental runs. The good activity exhibited by the catalyst was attributed to its large surface area and mesopores. The simple hydrothermal has also been demonstrated in Zn/La_2O_3 [55].

3.5 Catalyst reusability and leaching

Selection of material as heterogeneous catalyst for transesterification of vegetable oil is usually based on its catalytic activity and ability to be reused for subsequent experimental runs and also possesses potential ability to cater for low quality feedstock [34]. Leaching of catalyst active ingredients during transesterification is always the greatest concern. However, the reusability of the catalyst needs to be tested in order to check its stability and leaching behaviour. Calcium oxide (CaO) has been recognized as one of the catalysts that do not easily wash away by reaction medium [34]. Tan *et al.* [67] investigated the stability of CaO base catalyst derived from both chicken and ostrich

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eggshells by reusing the regenerated catalysts. The regenerated catalysts were able to be reused for five subsequent reaction cycles before deactivation set in. Although, the washing away of solid base catalyst is not avoidable, even soluble content in solid catalyst could be completely leached into reaction media during the reaction. This statement was corroborated by Kouzo *et al*. [97] who found out that some soluble ingredients were leached away from CaO based catalyst during methanolysis. However, during this process, CaO based catalyst reacts with glycerol under the same reaction conditions to produce calcium diglyceroxide which is highly reactive in the presence of water. Furthermore, the nature of oil used also determines the leaching activity of heterogeneous base catalyst, for instance, CaO based catalyst undergoes saponification reaction with oil containing high free fatty acid, which would deactivate the catalyst, reduce the biodiesel yield and make it difficult to separate biodiesel from product mixture [45]. This could be avoided by applying two-step transesterification process. More so, deactivation of catalyst could occur as a result of its exposure to carbon dioxide and moisture. When this happens, carbonate and hydroxide are formed. However, as suggested by Endalew *et al*. [32], adsorption of CO_2 on the catalyst surface can be avoided by polishing the surface of heterogeneous base catalyst with glycerol just after removal from reaction mixture. As for the moisture adsorption on catalyst surface, Nijiu *et al.* [98] found that calcination–hydration-dehydration is the appropriate treatment method to prevent CaO base catalyst from being converted to $Ca(OH)_2$.

In spite of the decline in activity of heterogeneous catalyst after use, its reusability could still be achieved by giving the regenerated catalyst proper treatment before subsequent use [45]. Generally, after a reaction cycle, the catalyst is separated from product mixture by means of filtration or centrifugation, follow by washing with solvent (methanol, ethanol, n-hexane) in order to remove physisorbed oil and then drying for long period. Tan *et al*. [67] examined the reusability of CaO base catalyst derived from chicken and ostrich eggshells. The authors treated the regenerated catalyst after each run by washing it with n-hexane to remove the adsorbed strains and later dried and recalcined at 700 ^{o}C for subsequent use. The catalyst was able to be reused for five reaction cycles and each run provide biodiesel yield around 75%. More so, Teixeira *et al*. [99] investigated the reusability of the K/MgO catalyst by washing the spent catalyst with methanol and recalcining at 700 ^{o}C. The catalyst was able to be reused for three consecutive runs without any decline in its activity. However, untreated spent catalyst showed very low conversion [99]. After these studies, the authors concluded that recalcination of used catalysts at elevated temperature after washing with solvent, maintains the catalytic activity and biodiesel yield during reuse.

3.6 Future research plan

The promotion of anthill-eggshell by mixed metal oxides has great fulfillment for biodiesel production from low grade feedstock. As discussed in the literature, the activity of bird eggshells increases with the impregnation of natural material or biomass on them [93, 100]. Likewise, modification of eggshell with mixed metal oxide would also improve its performance. Most of the stearate metals (Ca, Ba, Mg, Zn, Co, Ni, Mn, Cd, and Pb) are divalent and they tend to act as electron-acceptor via formation of a four membered ring transition state [40, 101-102]. A maximum yield of biodiesel (96%) was reported by Di Serio et al. [101] during transesterification of soybean oil with methanol over different stearate metal oxides. Although, both anthill and eggshell do transform into several metal oxides after thermal treatment at elevated temperature, but, only two stearate metals (calcium and small amount of magnesium) are present in those catalytic materials.

However, further research is required to get abundant results in using the anthill-eggshell promoted stearate metal oxides catalyst in biodiesel production. Another research which requires

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urgent attention involves mixed anthill clay (natural occurring item) and eggshell (waste) and its modifications for successful direct conversion of low-grade feedstock such as waste cooking oil and other non-edible oils into FAME by single-step transesterification method. Present two-steps transesterification technique for producing biodiesel from high free fatty acid (FFA) feedstock still not guarantee 100% conversion of triglyceride and complete removal of fatty acid. Currently, research has not been geared towards this direction. But the gathered research findings had shown that the use of modified composite material like mixed anthill-eggshell materials and its modification as heterogeneous catalyst for high FAME content yield is realistic.

4. Conclusion

Different forms of catalysts have been used for biodiesel production. Calcium oxide (CaO) is the most frequently used metal oxide catalyst for fatty acid methyl esters synthesis, due to its availability in abundance, non-toxic and ability to synthesize easily from waste materials. Amongst the various biodiesel production techniques reported in the literature, transesterification is the process adopted for the commercial production of biodiesel due to its simplicity. However, various heterogeneous catalyst preparation techniques were discussed. Catalyst reusability and leaching analysis were also a given special reference in this review. It was suggested that proper treatment of spent catalyst maintains the catalytic activity and biodiesel yield during reuse. The development of highly active heterogeneous catalysts from low cost, waste and naturally occurring materials for biodiesel production is so important since it provides a solution to the problems associated with the use of homogeneous catalysts and enzyme. Hence, researchers should focus on the development of economically viable as well as environmental friendly heterogeneous catalyst for biodiesel production.

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