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Research Article

An Insight into the Performance and Prospect of Catalysts in Biodiesel Production, with Special Emphasis on Heterogeneous Based Catalysis

Abdu Muhammad Bello[1*]

Department of Chemistry, Faculty of Sciences, Kano University of Science and Technology, Wudil, PMB 3244, Kano State, Nigeria

Corresponding author: muhbaf70@yahoo.com

ABSTRACT

Fossil fuel depletion, increased world energy demand, and the environmental crisis linked to petroleum-based energy instigated the quest for its substitute. The sustainability of biodiesel affords it a high prospect over fossil fuels. It has been receiving attention as a result of its biodegradability, renewability, low toxicity, and good transport and storage properties. The main shortcomings of biodiesel are the production cost and choice of catalyst. Three types of catalysts mainly used for biodiesel production are basic, acidic, or enzyme. Industrial production of biodiesel typically employed homogeneous catalysts due to their ability to facilitate the reaction quickly. However, catalyst separation and biodiesel purification are tormenting, requiring a large amount of water. Thus, heterogeneous catalysts, with several advantages over homogenous catalysts, have been searched. Heterogeneous catalysts can be separated from the products effortlessly, thus allowing for recycling. Furthermore, the process is simpler, cheaper, and more environmentally benign. This review aims to evaluate the performance of different types of catalysts in the transesterification reaction, with special emphasis on heterogeneous base catalysts. The review gives insight into the key catalytic properties that need to be tailored economically and eco-friendly to reduce cost, and give better biodiesel yield/conversion. Additionally, the various conditions necessary for the optimum yield of biodiesel have also been explored. The review highlighted that since single and mixed metal oxide catalysts suffered from low activity and instability, modifications need to be done by supporting alkaline or alkaline earth metals in such a manner that the supports hold the catalytic species firmly to achieve good reusability. The review also hinted that although alumina has been an excellent catalyst in many industries, it can only be used as catalyst support in transesterification reaction due to its low activity. The survey further discovered that the use of Nano-sized catalyst with high surface area and enhanced structural properties can help in achieving the key principles in the Green Chemistry. Furthermore, the review suggested solid catalysts, prepared from waste materials, for the reduction of overall biodiesel production cost. Lastly, the future challenges and prospects of heterogeneous base catalysts are proposed.

Keywords: Biodiesel, Catalyst performance, Heterogeneous catalyst, Transesterification

1. INTRODUCTION

The ever-increasing population growth, urbanization, and economic development continue to raise global energy demand. Further, the over-dependence on fossil fuels; such as coal, oil, and natural gas has significant environmental, economic, and geopolitical consequences [1-2]. These and other factors such as the rapid depletion of fossil fuel reserves, rising oil prices, and growing worries about greenhouse gas emissions in the atmosphere initiated the search for sustainable and environmentally benign alternative energy sources [3-6]. Biodiesel is one such option due to its green nature and other advantages over petroleum-based diesel [7-9]. In an early attempt, over 100 years ago, vegetable oil was proposed by Rudolf Diesel as an alternative to petroleum diesel [10]. However, vegetable oil is highly viscous and thus cannot function well in diesel engines [11]. For this reason, various methods have been investigated in an attempt to reduce the oil's viscosity. This includes pyrolysis, and micro-emulsification, among others [12]. Nevertheless, heavy carbon deposits due to incomplete combustion, coupled with the release of objectionable organic by-products, associated with these two methods have been a setback. Hence, transesterification has been the most efficient method of lowering vegetable oil's viscosity [13].

The transesterification product, known as 'biodiesel', can either be used purely or blended with petro-

diesel [13-15]. The renewability and green nature of biodiesel give it an edge over traditional petroleum diesel [16-17]. Its biodegradability allows for carbon dioxide recycling, thus significantly reducing the greenhouse effect [18]. Furthermore, biodiesel has a high cetane number, and high oxygen content, with no sulfur and aromatic compounds contained, thus their emission is cleaner [19-20]. Additionally, the energy density and kinematic viscosity of biodiesel-diesel blends are similar to the petro-diesel, and hence direct use in the existing engines is feasible [21-22]. The aforementioned advantages have sustained a growing interest in biodiesel production worldwide [23-25]. The global annual biodiesel production increased from 1.0 billion gallons in 2005 to 8.3 billion gallons in 2015 [26].

Catalysts in their simple or complex form, derived from a synthetic or natural source, are usually employed in a chemical reaction to speed it up [27]. Either homogeneous or heterogeneous catalysts can be employed in the production of biodiesel. Homogeneous catalysts used in transesterification reactions comprise HCl, H_2SO_4, NaOH, CH_3ONa, and KOH [28-30]. Nonetheless, homogeneous catalysis is both expensive and harmful due to high energy requirements, corrosion, and excessive use of water in the separation of the product from the catalyst [31-32]. Soap formation resulting from free fatty acids (FFAs} neutralization and triglycerides saponification are other setbacks of homogeneous catalysts.

Table 1: Homogeneous versus heterogeneously catalysts

Factors	Homogeneous Catalyst	Heterogeneous Catalyst
Conversion rate	Fast and high	Moderate
Oil to methanol ratio	Low	High
Continuous packed-bed	limited	Possible
Sensitivity water/FFAs	Not	Sensitive
Reusability	Cannot be reused	Can be reused
Cost	More costly	Cheaper
Selectivity	Limited	Possible

Consequently, heterogeneous catalysts have been introduced to resolve the flaws of homogeneous catalysts [33-34]. Heterogeneous catalysts have the capability of being reused, consequently their application in a packed bed reactor for industrial operation is feasible [35]. Such a reactor reduces the price of biodiesel by eliminating the separation stage [28, 22]. Furthermore, heterogeneous catalysts benefit from high activity, selectivity, and a long catalyst lifetime [36-37]. The homogeneous and heterogeneous catalysts are compared in Table 1 for easy discernment of their advantages and disadvantages. The review focusses mainly on the synthesis of highly efficient heterogeneous catalyst with good stability to enhance

biodiesel production. It evaluates the development and production of various heterogeneous base catalysts from different sources including waste materials to reduce biodiesel cost globally. It also envisages the future and prospect of catalysts.

2. MATERIALS AND METHODS

Original research papers (mainly peer-reviewed papers) and reviews were used for this literature survey. The summary of the works consulted in this review according to year of publication is presented in Figure 1 to signify the prevalence of the study. The figure indicates the currency of the review as most of the papers reviewed are within the range of 2015 to 2024 year of publication, with very few old publications, mainly to provide a better understanding of the concept of catalysis in biodiesel production. This justifies the ability of the review in proposing future catalysts that can reduce the biodiesel cost.
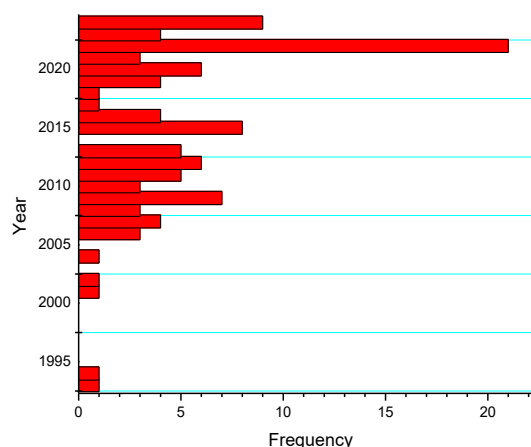

Fig. 1. Bar graph of the reviewed literature
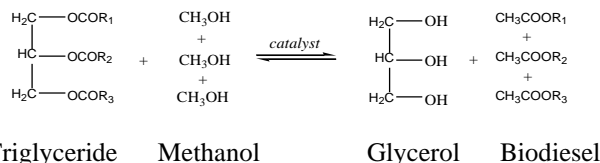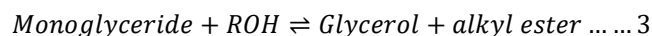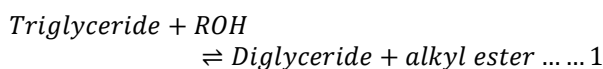
3. BIODIESEL PRODUCTION

The environmental menace connected to fossil fuels, the rise in energy demand, and the decline in fossil fuel reserves, among others, impelled the quest for alternative sources [38-41]. Biodiesel has been proven to be a promising preference for petro-diesel [42-43]. The production of biodiesel is via the transesterification of oils and fats, thus, the emission of greenhouse gases is drastically reduced [44-45]. The methods commonly employed in transesterification are mainly; batch process, supercritical process, ultrasonic method, and microwave method.

Biodiesel is frequently produced by the methanolysis or ethanolysis of high molecular weight fatty acids [35]. Although high molecular weight alcohols, such as isopropanol and butanol, are equally used to boost the

biodiesel's cold flow property, the reaction is less efficient [15]. Some of the advantages of biodiesel are high; flash point, lubricating efficiency, and cetane number with no sulfur content. Furthermore, biodiesel's combustion properties are comparable to petroleum diesel [15,46].

4. TRANSESTERIFICATION REACTION

Transesterification is the alcoholysis of an ester in a process that involves the replacement of its alcohol with another alcohol [47]. Biodiesel was incidentally invented in an attempt to extract glycerol needed for the manufacture of wartime explosives from soap by-products, this research was patented in the early 1940s [48]. The three consecutive and reversible steps involved in the transesterification reaction are presented in Equations 1-3, while the overall reaction is shown in Scheme 1 [49]. The scheme signified that every 1 mole of triglycerides required 3 moles of alcohols to produce 3 moles of biodiesel (alkyl ester) with a mole of glycerol as by product. In addition, heat and catalyst are necessary to speed up the reaction.

$$Triglyceride + ROH \rightleftharpoons Diglyceride + alkyl\ ester \ldots\ldots 1$$

$$Diglyceride + ROH \rightleftharpoons Monoglyceride + alkyl\ ester \ldots\ldots 2$$

$$Monoglyceride + ROH \rightleftharpoons Glycerol + alkyl\ ester \ldots\ldots 3$$

Triglyceride   Methanol   Glycerol   Biodiesel

Scheme 1. Overall transesterification process

Even though, the stoichiometric amount of alcohol in the overall process is three, an excess of 3 moles is necessary to attain a high yield. Despite that, the number of moles of alcohol should not be in too much excess for easy separation of the products [47]. Thus, for homogeneous catalysis 6 moles are suggested, while 15, 40, and 275 are recommended for heterogeneous catalysis to improve the transesterification rate and simplify the catalyst's active site regeneration [50].

4.1   Mechanism of Acid Catalysis in Transesterification

The mechanism of an acid catalyzed biodiesel production is expressed in Scheme 2. The process begins with the protonation of ester to produce carbonion ions. Then the carbonion ion undergoes rearrangement and is in turn attacked by a nucleophile (alcohol) to give a tetrahedral intermediate. This is followed by the elimination of a glycerol to form an alkyl ester (biodiesel). The process is

repeated until all the esters are protonated and converted into alkyl esters.
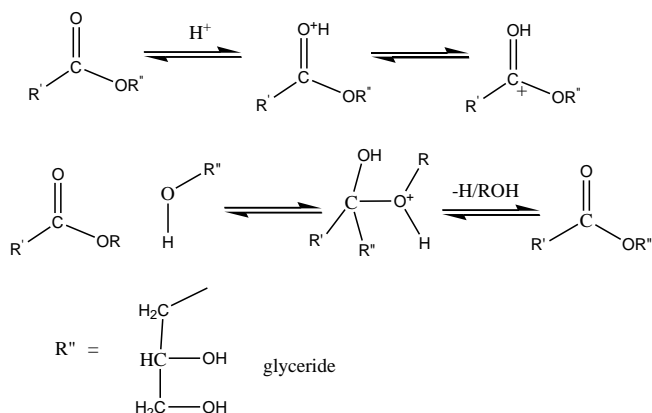
Scheme 2. of acid catalysis in transesterification steps [48]

4.2   Mechanism of Base Catalysis in Transesterification

Due to its faster reaction rate and corrosion free activity, basic catalyst is preferable in industrial processes over the acid counterpart [51]. In this process, the alcohol and catalyst in the reaction mixture react to generate alkoxide ions, initiating the reaction [48]. The various steps involved are illustrated in Scheme 3. Immediately the alkoxide ion is formed. it attacked the triglyceride at C=O double bond and generate an intermediate. This is followed by the elimination of an alkyl ester molecule and regeneration of the catalyst. The process is repeated until all the remaining 3 molecules of the alkyl esters are formed.
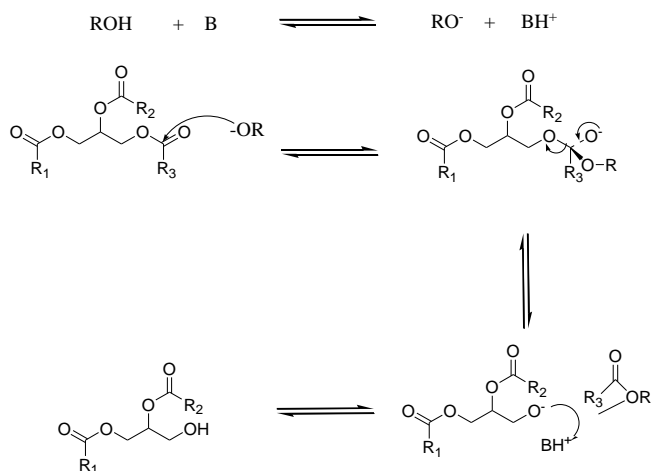
Scheme 3. Outline of base catalysis in transesterification [47].

5. GENERAL MECHANISM OF HETEROGENEOUS CATALYSIS

It is a well-established reality that a catalyst acts by providing an energetically favorable pathway for the

reacting molecules. Generally, the reactants are adsorbed onto the catalyst surface, then the intramolecular bonds are broken or weakened, followed by the reaction of the molecules often in several consecutive steps. For instance, in the oxidation of CO, the catalyst adsorbed the CO and O_2. This is followed by dissociation of the O_2 bond, due to the decrease in potential energy as the adsorption is exothermic, to give two O atoms. Subsequently, the CO and O unite to form adsorbed CO_2 molecules. Finally, the CO_2 molecule is desorbed immediately liberating the catalyst's surface for the next reaction cycle as demonstrated in Figure 2. The regeneration of the catalyst's active sites distinguished catalytic reactions from stoichiometric reactions [52].
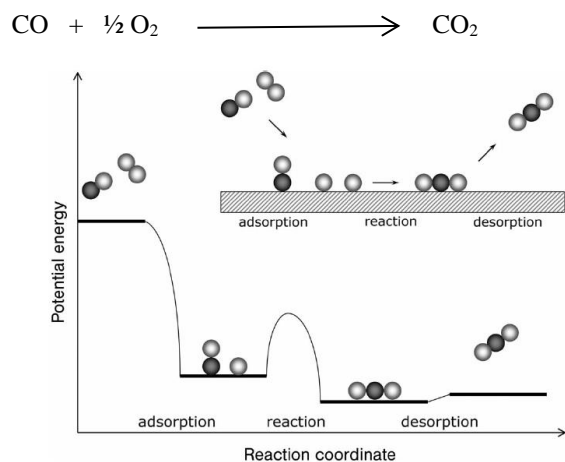
$$CO\ +\ \tfrac{1}{2}\,O_2\ \longrightarrow\ CO_2$$

Fig. 2. Catalytic oxidation of carbon monoxide [52]

Similarly, the heterogeneous transesterification mechanism can be explained in the same way. The alcohol adsorbed onto the catalyst surface generating highly active alkoxide ions. The alkoxide ions are then combined with adsorbed glycerides to produce methyl esters. This is followed by instantaneous desorption of the methyl esters, allowing for regeneration of the catalyst's surface. At the commencement of the reaction, the glyceride adsorption is controlled by external mass transfer limitations, while the later reaction is governed by the reaction of the alkoxide ion and TG [52].

6. HETEROGENEOUS ACID CATALYSTS

Heterogeneous acid catalysts were developed to curb, inter alia, the corrosion problems and ensuing environmental threat of homogeneous counterparts. However, the reaction rate of heterogeneous acid catalysts is slow and the reaction is connected with unfavorable side products. Furthermore, understanding the parameters controlling solid acid catalyst activity is still vague. For instance, the relationship between acid strength and catalyst activity is yet to be established. Secondly, even though the synthesis of a heterogeneous acid catalyst having interconnecting pores that will promote

transesterification reaction was achieved, the control of the catalyst's pore size, diameter, morphology, as well as stability is not easy [15].

Solid acid catalysts used in transesterification reactions include; zeolites, tungsten oxides, sulfated zirconia (SZ), sulfonated saccharides, Nafion1 resins, phosphoric acid modified mordenite (PMOR), and mesoporous organosulphonic functionalized silica. Although solid acid catalysts are efficient in the esterification of carboxylic acid, lower activity necessitates higher reaction temperatures for their application in the transesterification reaction. However, some resins with a high number of acid sites are exceptional as they have appreciable activity for both carboxylic acid esterification and FFAs transesterification. Nevertheless, thermal stability hinders the application of the resin-type catalysts in reactions, such as reactive distillation, that require higher temperatures. Another concern is associated with catalyst regeneration [15]. Due to all these shortcomings, heterogeneous base catalysts have been introduced. Thus, the current review will be centered on heterogeneous base catalysis in transesterification reactions.

7. HETEROGENEOUS BASE CATALYSTS

Heterogeneous base catalysts came much later than their acid counterparts. The first report on the solid base catalyst was by Pines and Haag. The catalyst composed of Na metal supported on alumina, was found to be efficient in the isomerization of alkenes. The studies on solid base catalysts have made far-reaching progress since the publication of a book by Tanabe, titled "Solid Acids and Bases" [53]. The Brønsted site of heterogeneous base catalyst abstracts proton from the reactant and the Lewis basic site donates an electron to the reactant. Some of the advantages of this catalyst are; higher activity, longer catalyst lifetime, milder reaction conditions, and a reaction rate that is about 4000 times higher than the acid equivalent [47]. The active sites of solid base catalysts can activate reactants with or without proton abstraction.

7.1 Activation of the reactant with proton abstraction

According to Equation 4, the proton of the reactant molecule is abstracted to form carbanion when this molecule is adsorbed on the catalyst surface.

$$\underset{Molecule}{AH} + \underset{Basic\ Sites}{B^-} \rightarrow \underset{Carbanion}{A^-} + BH \dots\dots 4$$
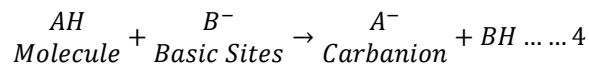
For molecules with high pKa values, strong base catalysts are used for easy proton abstraction. For instance, in alkane isomerism, the first step is the abstraction of protons leading to the formation of carbanion as shown in Scheme 4.
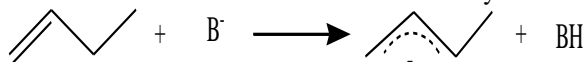
Scheme 4. Activation with proton abstraction

7.2 Activation of reactant without proton abstraction

Carbonyl compounds are usually activated without proton abstraction as shown in Scheme 5. An example of this type of reaction is aldol-condensation.
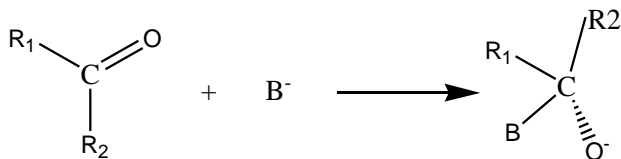
Scheme 5. Activation without proton abstraction

Different categories of heterogeneous basic catalysts are employed in transesterification reaction, details of these catalysts are discussed in the succeeding subsections.

7.3 Metal oxide catalysts

Metal oxide catalysts can either be single (e.g. MgO, CaO, ZnO, etc.), or mixed composed of metal of group I, II, or rare earth metal with transition elements oxides (e.g. BaCeO$_3$). The cation of the metal oxides possesses Lewis acid and the anion possesses Brønsted [54-55]. In a study, Tahvildari *et al* (2015) synthesized Nano CaO and MgO catalysts and evaluated their activity in biodiesel production [56]. The Nano CaO was found to perform better under milder reaction conditions, with higher yield and recyclability than the Nano MgO catalyst. This was connected to the better basicity and surface structure of the Nano CaO. However, when mixed in different proportions with Nano CaO, improvement in the basic properties of the Nano MgO was observed, resulting in an increased biodiesel yield. Accordingly, a 98.95% yield was obtained using a 0.7: 0.5 CaO to MgO mixture, with better repeatability than the Nano CaO alone. In an analogous study, Esmaeili et al., (2019) synthesized MgO nanocatalyst and applied it in the transesterification of low-cost Moringa oleifera seeds oil [57]. The result of the catalyst characterization revealed heterogeneous, asymmetrically distributed small particle sizes. The presence of a great number of pores and inter-mass gaps on the catalyst's surface offers available sites for the transesterification process to occur. Thus, up to 93.69% yield of biodiesel was realized with 1 wt% catalyst, at 45 °C, for 4 h, and a 1:12 molar ratio.

In a related study, Sulaiman *et al.* (2020) synthesized CaO nanoparticles by thermal decomposition of commercial calcium carbonate, CM-CaCO$_3$, under a vacuum atmosphere, by varying the temperature (100 °C to 700 °C) [58]. The FTIR result specified a complete formation of CaO at 700 °C, which is affirmed by the XRD result that revealed peaks exclusively due to crystalline cubic CaO, and the absence of peaks associated with rhombohedral CaCO$_3$ plus hexagonal Ca(OH)$_2$. Interestingly, the surface area and basicity, respectively 11.5 m^{2}g^{-1} and 1.959 mmol/g, are the highest for the CaO-700 catalyst. The high basicity was attributed to an increase in O^{2-} centers at elevated temperatures of calcination, due to the elimination of OH centers that covered the CaO nanoparticles' surface. When tested in rice bran oil methanolysis, up to 89.0% yield was achieved in 60 minutes, with only 0.5% catalyst amount. In a parallel study, methanolysis of *Balanitea egyptiaca* (Desert date) seeds oil catalyzed by CaO was reported. The yield reached 96.3% with 0.4% catalyst loading, at 55 °C, for 1 h. The high biodiesel yield was confirmed by the FTIR spectrum of the biodiesel that depicted a sharp band of O-CH$_3$ around 1033 cm^{-1}. This peak was absent in the Desert date oil spectrum [59]. A similar study reported the synthesis of CaO nano-catalyst using calcium nitrate tetrahydrate as precursor by thermal-decomposition method, the catalyst was calcined at 500 °C followed by characterization using X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. The XRD results revealed nano-scale crystal sizes with high purity, a mean particle size of around 29 nm, and very good crystallinity.

From the SEM analysis, the catalyst exhibited particles with irregular shapes and porous structures. The catalyst's activity was evaluated in a transesterification reaction, by varying the catalyst's loading and oil: methanol ratio; 0.5 to 5%, and 1: 4 to 1: 10, respectively. The biodiesel yield increased with the catalyst's loading from 0.5 to 1% w/w then declined with further increment, and with molar ratio from 1:4 to 1:8. Consequently, the highest conversion of 96% was achieved at optimized experimental conditions; 50 °C, 1:8 oil to methanol ratio, 1 wt% of catalyst and 90 min reaction time. The work asserted that the reported synthesis method for the nano-CaO catalyst was uncomplicated, entailing only preparation and activation by calcination. Furthermore, it claimed that the catalyst is economical, environmentally benign, and easy to handle, with high basicity and low solubility allowing for the catalyst's reusability [60].

In an attempt to improve the activity and stability of the single metal oxide catalysts research has been shifted to the synthesis of mixed metal oxides. Correspondingly, a study reported the synthesis of mixed CaO-MgO catalyst using the co-precipitation method, to correct the instability associated with CaO and improve its activity. The Mg-doping was varied to determine the best ratio of Mg: CaO for optimum performance. The activity of the different catalysts was investigated in the transesterification of

soybean oil. The characterization results proved the presence of Mg in the doped sample. The Mg doping reduced the lattice spacing of CaO, improved the intensity and number of basic sites, and enhanced the activity of the catalyst, thereby improving the FAME yield from 57.6% for the pure CaO to 98.3% for the Mg-doped CaO catalyst in the ratio of 1: 3, under the reaction condition: 60 °C, 1: 12 oil: methanol ratio, 1.5 wt% of catalyst, and 2 hrs. reaction time. This was achieved even though supporting MgO on CaO may result in poor pore structure, thus weakening the adsorption and diffusion of reactant molecules to the basic sites, and lowering activity. The optimal performance displayed by 1: 3 Mg: Ca catalyst was credited to higher Mg doping and suitable surface area. The catalysts also proved good stability, as the FAME yield exceeding 80% was maintained after the 5th cycle. The catalyst's stability was attributed to the protection of the basic sites on the catalyst's surface from water and CO_2 contamination by the Mg-doping, which are the main causes of the catalyst's deactivation [20].

Another research by Sahani et al., (2019) reported the synthesis of mixed oxide of barium and cerium by sol-gel method [61]. To investigate the active phase present in the perovskite $BaCeO_3$ catalyst, the calcination time and stoichiometric ratios of Ba: Ce were optimized. Eventually, 1:1 Ba: Ce catalyst calcined for 3.5 hours gave the highest FAME conversion of 98.41% in Karanja oil transesterification using 1.2 wt % catalyst loading, 1:19 molar ratio, 65 °C, 100 min, and 600 rpm agitation speed. The excellent conversion was ascribed to the higher basicity possessed by the catalyst, the maximum exposed area on the catalyst's surface, plus the well-packed and ordered particles of the perovskite that facilitated reactants' adsorption on the catalyst's surface. Furthermore, the catalyst has excellent reusability with 81% conversion after the sixth cycle. This was attributed to the strong intermetallic linkage, Ba-O-Ce, that prevented the leaching of the catalyst. Conversely, the lower activity of the 1:2 Ba/Ce catalyst was attributable to the formation of the inactive CeO_2 phase alongside the active $BaCeO_3$. A similar study reported a green synthesis of GO-$CuFe_2O_4$ nanocomposite as an organo-base functionalized high surface area magnetic nanocatalyst using a mixture of $CuCl_2 \cdot 2H_2O$ and $FeCl_3 \cdot 6H_2O$ as precursors, Graphene oxide (GO) as modifier, and pistachio leaves extract as structure directing agent.

The SEM micrograph of GO-$CuFe_2O_4$ displayed assembled particles and sheet morphology. The EDX result indicated that the catalyst contains Fe and Cu as metallic and C, N, O as non-metallic components. Subsequently, the catalyst was tested in the transesterification of rapeseed oil and waste corn oil. The optimum conditions for biodiesel production were determined through response surface methodology based on Box–Behnken design by varying catalyst loading, methanol to oil molar ratio, and reaction time. The catalyst loading was found to be the most influential parameter for both rapeseed oil and waste-corn oil transesterification. The respective optimum yields of

biodiesel for rapeseed oil and waste-corn oil were 92.81% and 87.26%, under reaction conditions: 8 wt% of catalyst, 13:1 methanol: oil molar ratio, and 7 h of reaction time [62]. Table 2 summarizes the various metal oxides catalysts reviewed and the respective optimum biodiesel yields realized.

Table 2: Summary of metal oxides catalysts

Catalyst	Optimum yield (%)	Reference
Nano CaO and MgO	98.95	[56]
MgO Nanocatalyst	93.69	[57]
CaO Nanoparticles	89.0	[58]
Commercial CaO	96.32	[59]
CaO Nanocatalyst	96	[60]
CaO-MgO mixed catalyst	98.3	[20]
$BeCeO_3$ perovskite	98.41	[61]
Graphene oxide GO-$CuFe_2O_4$ nanocomposites	92.81	[62]

7.4 Supported Base Catalysts

During catalyst preparation, supports are modified to hold catalytic species firmly to achieve reusability. The most commonly used catalyst supports include; MgO, CaO, ZnO, and Al_2O_3. Alumina is the most popular among these supports due to its high resistance to heat, large surface area, porosity, mechanical stability, availability, as well as low density, and cost. Due to their super basicity, group I and II metals and their salts, are usually doped onto these supports to improve the number of active sites. For example, when Al_2O_3 was doped with KNO_3, Al-O-K active species were generated by replacing the proton of the $Al(OH)_3$ with K^+ ions, while K_2O are generated by subsequent calcination. The number of basic sites depends on the amount of dopant and the temperature of calcination [28]. The reports on supported base catalysts are discussed in the subsequent paragraphs, while the review intends to take the discussion on alumina-supported basic catalysts into a separate subsection due to their versatility.

A study reported the preparation of nanocrystalline ZnO doped with 2.26% (wt.) potassium by precipitation method. The catalyst gave 89.20% biodiesel yield in rice bran oil transesterification under the RSM model's suggested optimal conditions; 3.60 %wt. Catalyst loading, 65 °C, 120 mins., and a molar ratio of 6. The researchers concluded that since only 2.26% of K was detected in the biodiesel for the leaching test, the reaction can be considered as heterogeneously catalyzed with very little contribution from the leached K. Consequently, the catalyst was able to be recycled three more times before deactivation [63]. In a parallel study by Roy et al., (2020), La_2O_3 was promoted with potassium and applied in castor oil methanolysis. The

catalyst prepared with a 1.5: 1 atomic ratio of K: La and calcined at 900 °C gave a high conversion of 97.5% with 2 wt% catalysts, 16: 1 molar ratio, at 65 °C, for 150 min, and 500 rpm stirring rate [64]. The generated active K_2O and K_2CO_3 along with the pure La_2O_3 phase, coupled with the homogeneously dispersed and less aggregated particles possessed by the catalyst, contributed to the enhanced basic strength desirable for the transesterification process. Furthermore, the catalyst exhibited good reusability with up to 85.3% FAME conversion after the fifth cycle. The decrease in conversion with catalyst's recycle was attributed to the leaching of K_2O and K_2CO_3.

In a related study by Bambase Jr *et al.*, (2021), CaO was wet impregnated with NaOH (10-20%, w/v), and calcined at 550 ºC - 700 ºC for 2 - 5.5 h [65]. The catalyst prepared with 20% NaOH, at 600 ºC for 2 h gave up to 66.36% biodiesel conversion from refined coconut oil in just 10 min, while the reaction catalyzed by untreated CaO took a longer time to commence. The fast reaction rate of the OH-modified catalyst is a result of the high specific surface area originated from the well-shaped lumps of tiny porous particles that served as the basic sites. While the slow catalytic activity of the untreated CaO was attributed to the presence of $CaCO_3$ phase that was believed to compete with the active CaO and $Ca(OH)_2$ in the catalyst's structure. Table 3 is examples of supported base catalysts with their optimum biodiesel yields.

Table 3: Summary of supported base catalysts

Catalyst	Optimum yield (%)	Reference
Zn doped K	89.20	[63]
La_2O_3 promoted with K	97.5	[64]
CaO doped NaOH	66.36	[65]

7.5 Alumina as catalyst support in transesterification

Alumina exists as γ-, η-, σ-, θ-, κ-, χ-, or α-Al_2O_3. Due to its excellent physical, chemical, thermal, and textural properties, alumina has been utilized as a catalyst or catalyst support. These properties permit high doping of active phases [67-69]. Thus, alumina is the most frequently used catalyst support owing to its high surface area and thermal stability. However, alumina has low activity in transesterification reactions, thus, the need to modify its properties for improved activity. On account of its amphoteric nature, both the acid and basic sites of the alumina can be modified [28, 70]. Table 4 portrays a summary of the literature surveys on various acid and base-supported alumina catalysts for transesterification reactions. However, since the review is more concerned with heterogeneous basic catalysis, the later discussion will be on alumina-supported basic catalysts.

Table 4: Generation of Acid and Basic Sites on Alumina

Catalyst	Remark	Reference
$H_4SiW_{12}O_{40}/Al_2O_3$	Acid site	[71]
s-MWCNTs	Acid site	[72]
$HSiW$-ZrO_2	Acid site	[73]
SO_4^{2-}—ZnO	Acid site	[74]
NiW/SiO_2-Al_2O_3	Acid site	[75]
HSiW/SBA-15	Acid site	[76]
SO_4^{2-}/Al_2O_3-SnO_2	Acid site	[77]
MoO_3/Al_2O_3	Acid site	[78]
Nb_2O_5/Al_2O_3	Acid site	[79]
Nb_2O_5/Al_2O_3	Acid site	[80]
In_2O_3-Al_2O_3 & Ga_2O_3-Al_2O_3	Acid site	[81]
TiO_2/Al_2O_3	Acid site	[82]
KF & $NaNO_3/Al_2O_3$	Basic site	[83]
$CaO/KI/Al_2O_3$	Basic site	[84]
KI/Al_2O_3	Basic site	[85]
CaO/Al_2O_3	Basic site	[86]
$NaOH/Al_2O_3$	Basic site	[87]
KF/Al_2O_3	Basic site	[88]
$NaOH/Al_2O_3$	Basic site	[89]
KI/Al_2O_3	Basic site	[90]
$Na/NaOH/\gamma$-Al_2O_3	Basic site	[91]

7.6 Base-supported alumina catalysts in biodiesel production

As earlier highlighted, alumina is the most extensively used catalyst support because of its exceptional thermal, mechanical, and structural properties. Thus, numerous reports are available on base-supported alumina catalysts in the production of biodiesel. One such study by Xie et al., (2006), reported the synthesis of Al_2O_3-supported catalysts by varying amounts of different potassium salts (KF, KCl, KBr, KI) [90]. The Al_2O_3 doped with 35 wt% KI and calcined for 3 h at 500 ºC was the best catalyst, with up to 96% biodiesel yield, under the conditions of 2.5% of the catalyst, 15:1 molar ratio, and 8 hours reaction time. The higher activity of KI/Al_2O_3 was linked to the lower thermal stability of KI compared to KBr and KCl, resulting in the easy formation of active K_2O species. On the other hand, the superior activity of KI/Al_2O_3 over KF/Al_2O_3 catalyst may be explained by the fact that the active species, F^-, in KF/Al_2O_3, may be weaker than K_2O basic sites. In another study, D'Cruz et al., (2007) promoted alumina with K_2CO_3 and tested it in the methanolysis of canola oil[92]. This catalyst performed better than catalysts prepared by promoting CaO, BaO, and MgO with Li, Na, and K, yielding up to 94.2% ester under the suggested RSM model's reaction conditions of; 11.48:1 molar ratio, 60 ºC temperature, and 3.16 wt.% catalyst. The high catalytic activity associated with the K_2CO_3/Al_2O_3 catalyst may be attributed to the possession of a much higher surface area of 118 m^2/g, and high basicity. In their study, Arzamendi et al., (2007) prepared calcined

and un-calcined NaOH/Al$_2$O$_3$ catalysts and compared their activity in sunflower oil methanolysis [89]. The calcined catalyst gave a yield of 86%, while the un-calcined catalyst accomplished a 99% yield, under the same reaction conditions; 12:1 molar ratio, for 24 hours. However, the higher yield achieved with the un-calcined catalyst could be associated with homogeneous contribution due to the non-conversion of the NaOH into Na$_2$O.

In a parallel study, Boz & Kara, (2009) prepared alumina and modified it with 30 wt.% of KI, KF, K$_2$CO$_3$, or KNO$_3$ [88]. The catalyst modified with KF had the highest activity yielding up to 99.6% biodiesel from canola oil under the conditions; 15:1 molar ratio, 3 wt.% catalyst, 60 °C, and 8 hours. The high activity of KF-Al$_2$O$_3$ was attributed to the high surface area, enhanced basicity, as well as well-dispersed KF that form a monolayer on the alumina. The K$_2$O and Al-O-K formed by KF decomposition contributed to the high basicity and activity of KF-Al$_2$O$_3$. Furthermore, Anderson et al., (2009) synthesized BaO/Al$_2$O$_3$ catalyst with different baria loading (1, 2.5, 5, and 10 wt.%) and assessed the activities in a transesterification reaction [93]. The result revealed a complex relationship between transesterification reaction and baria dispersion, with low-dispersed samples showing better sensitivity to FFA than poor-dispersed. Accordingly, it was suggested that for high FFA oils, better-dispersed catalysts are more appropriate.

In another study, Istadi et al., (2010) wet-impregnated alumina with different amounts of LiNO$_3$ (10 to 40 wt%) and used it to catalyze palm oil methanolysis [94]. The 20 wt.% LiNO$_3$ catalyst showed well-dispersed particles, resulting in stronger adsorption of reactant, hence, the highest conversion of 97.8 wt% was achieved. For catalysts with less than 20 wt% loadings, the basic sites were very low for the methanolysis reaction to occur. However, when the amount exceeded 20 wt%, the surface area decreased due to particle agglomeration leading to the lowering of the number of basic sites. In a related study, Taufiq-Yap et al., (2011) doped Al$_2$O$_3$ with various amounts of NaOH and applied it in palm oil methanolysis [87]. The catalyst prepared with 50 wt% NaOH had the highest yield of 99% when the methanolysis was carried out with 3 wt% catalysts, at 60 °C, for 3 hours, and 1:15 molar ratio. Nevertheless, the fact that a high amount of NaOH loading was used in the catalyst's modification, implied a possible homogeneous catalytic contribution to the process. This assertion is true since the study confirmed the formation of sodium aluminate due to a reaction between the alumina support and high-loaded NaOH.

In an attempt to improve on the single-promoted alumina catalysts, Kim et al., (2004) double promoted γ-Al$_2$O$_3$ with varying amounts of Na and NaOH, then tested it in soybean oil transesterification [91]. The Na/NaOH/γ-Al$_2$O$_3$ catalyst doped with 20 wt.% of both Na and NaOH has the highest yield of 94% using a 1 g catalyst and a 9:1 methanol to oil ratio. The high activity was credited to the generation of sodium aluminate from the reaction of sodium

hydroxide and the γ-Al$_2$O$_3$ support, and the ionization of sodium. In a parallel study, Ma et al., (2008) varied the K and KOH wt.% supported on γ-Al$_2$O$_3$ and tested the activities in rapeseed oil methanolysis [95]. The 7.5%-K/20%-KOH/γ-Al$_2$O$_3$ catalyst gave a maximum of 84.52% yield, using 4 wt.% of the catalyst, 1:9 molar ratio, at 60 °C, for 1 hour, and a stirring rate of 270 rpm. The activity of the catalyst was a result of the active orthorhombic β-KAlO$_2$ species formed. Nevertheless, the slow stirring rate employed in this study could be the reason for the not-so-high conversion, since the optimum stirring rate was reported to be around 600 rpm.

A parallel study by Asri et al., (2012) reported the double-promotion of γ-alumina catalysts by the co-precipitation of CaO (10 to 50 wt.%) and Al$_2$O$_3$ followed by impregnation with 35 wt% KI [84]. The 30%-CaO/35%-KI/Al$_2$O$_3$ calcined at 650 °C for 4.5 hrs was the most active catalyst. It gave almost 95% yield using 6 wt% catalysts in the methanolysis of palm oil at 65 °C, for 5 h, and a 1:42 oil/methanol ratio. The lower yield with CaO loading exceeding 30% was credited to the covering of the basic sites and the consequent surface area lowering due to particle agglomeration. The fact that the optimum activity was achieved at 650 °C calcination temperature was ascribed to the fact that elevated temperature is essential for the removal of surface water and carbon dioxide on the calcium oxide to enhance the number of basic sites. Furthermore, at high temperatures, the Ca^{2+} and O^{2-} on the surface of calcium oxide assumed a coordination state that favored high activity. However, the high molar ratio reported could make biodiesel separation from glycerol difficult.

From the foregoing survey, it is clear that most of the reported literature employed commercial or microporous alumina as support. These aluminas suffer from a low surface area that may hinder catalytic activity. Further, the times reported for the transesterification reaction to complete using these alumina-supported catalysts, as well as the metal oxides and metal oxides-supported catalysts, are unusually high (3 hours and in some cases up to 24 hours). This indicated low catalytic activity and a slow reaction rate. To overcome these setbacks, mesoporous alumina was synthesized and wet-impregnated with 5 to 25% NaOH to ascertain the effect of the catalyst's particle size and number of active sites on the methanolysis of corn oil. The parameters for the methanolysis were optimized using the Box-Behnken Design (BBD) model. As high as 96.1% conversion was obtained with 6% of 15%-NaOH/Al$_2$O$_3$ catalyst, at 65 °C, using a 1:15 molar ratio, within 2 hours of reaction time [96]. The fact that only 15% NaOH was used in the catalyst modification to achieve very high biodiesel yield in a shorter reaction time, affirmed the claim that using mesoporous alumina can improve catalytic activity and accelerate reaction rate. This is true since from the aforementioned pieces of literature 30% and above loading was employed when microporous alumina was used as support. Since the literature established that catalysts

modified with alkali metals usually suffer from leaching of the active site, a leaching test was conducted on this catalyst. The catalyst was found to be moderately stable with only 0.7% of Na_2O leaching. Furthermore, the lixiviation test revealed only a 13.5% FAME yield, thus, the leached Na_2O contributed negligibly to the catalytic process. The study attributed the catalyst deactivation to particle agglomeration observed from the SEM image [97]. Table 5 summarizes the performances of various base supported alumina catalysts.

Table 5: Summary of base supported alumina catalysts

Catalyst	Optimum yield (%)	Reference
KI/Al_2O_3	96	[90]
K_2CO_3/Al_2O_3	94.2	[92]
$NaOH/Al_2O_3$	99	[89]
KI, KF, K_2CO_3, or KNO_3/Al_2O_3	99.6	[88]
BaO/Al_2O_3	Not reported	[93]
$LiNO_3/Al_2O_3$	97.8	[94]
$NaOH/Al_2O_3$	99	[87]
$Na/NaOH/Al_2O_3$	94	[91]
$K/KOH/Al_2O_3$	84.52	[95]
$CaO/KI/Al_2O_3$	95	[84]
NaOH/mesoorous-Al_2O_3	96.1	[97]

7.7 Waste-derived catalysts

High production cost, in terms of feedstock oil and catalyst acquisition, is one of the major challenges facing the global commercialization and acceptance of biodiesel. Consequently, for biodiesel to compete favorably with petroleum diesel economically, attention has been shifted to the use of waste materials as precursors for catalyst synthesis. This practice will not only help in reducing the price of biodiesel but also help in reducing the environmental nuisance caused by the dumping of these wastes, among others [12]. This is because effective solid waste management leads to a healthier environment and the generation of this solid waste is something that cannot be avoided [98]. Along this line, a CaO-doped KF catalyst was prepared starting with eggshells calcination in air at 820 °C for 4 hours, then impregnation with KF. When used in a methanolysis reaction as high as 94.2% FAME yield was achieved with 1 wt% of 5%-KF/eggshell catalyst, at 50 °C, for 1 hour, and a 1:6 molar ratio. The high activity was attributed to an improved saponification resistance and the contribution from the well-distributed $KCaF_3$ active crystals on the catalyst's surface. The F^- in $KCaF_3$ served as a strong Lewis base hence easily obstructing H^+ from CH_3OH to form CH_3O^-. Additionally, the strong Lewis acid Ca^{2+} improved the CH_3O^- adsorption on the KF/eggshell catalyst. Consequently, the CH_3O^- easily attacked the triglyceride, resulting in a high FAME yield. Thus, the study concluded

that the catalyst is simple, economical, efficient, and promising [99].

To tailor the structural properties of CaO derived from waste eggshells to improve catalytic activity, a study reported the synthesis of CaO nano-catalyst by calcination of eggshell powder at 900 °C followed by hydration-dehydration treatment. The presence of sharp peaks associated with CaO in the XRD diffractogram confirms the formation of CaO. The XRD result further suggested that the hydration dehydration treatment has a strong effect on the crystallinity and crystalline size of the catalyst. The treatment considerably decreases crystallinity thereby increasing porosity and crystalline size, as a result, the surface area increased. This could be associated with the evolution of water molecules since the removal of the water molecules from the lattice during calcination of the hydrated samples ruptures the crystallites. The EDX analysis revealed calcium and oxygen with respective 54.74 and 39.76 mass percentages are the major constituent of the eggshell-derived CaO nano-catalyst. After the hydration-dehydration treatment, the morphology of the catalyst changed from rod-like to honeycomb-like porous microstructure. Likewise, average particle size was reduced from 21.30 to 13.53 nm, leading to an increase in surface area. The change in morphology with hydration-dehydration treatment could be connected to the release of water molecules during the decomposition of $Ca(OH)_2$, thus creating high porosity and more activity. Besides, the hydration-dehydration treatment leads to more uniform textural properties. Accordingly, the highest biodiesel yield of 94% was obtained at 1:12 oil to methanol molar ratio, 2.5 wt% catalyst loading, 60 °C, and 120-min reaction time. The research emphasized that the synthesis procedure is promising for the development of cheap and green technology [100].

In a recent study, Miladinovic et al., (2020) calcined walnuts shell at 800 °C in air and investigated their activity in sunflower oil methanolysis [101]. The catalyst consisted mainly of CaO, K_2O, and MgO, implying high basic nature. Consequently, above 98% yield was accomplished with 5% catalyst in barely 10 min, at 60 °C, and 1:12 molar ratio. The research concluded that even though the walnut shell ash calcination requires high energy, nevertheless, the heat/electricity generated, and averting of operating cost on walnut shell ash disposal, may reimburse the high energy cost. In another study, Pavlović et al., (2020) developed a novel environment-friendly CaO/FA-ZM catalyst using hydration-dehydration in a miniature autoclave. The active CaO and FA-ZM were derived from waste eggshells and lignite coal fly ash, respectively. When 6 wt% of the catalyst was tested in a methanolysis reaction, very high activity with 97.8% FAME conversion in only 30 min, using a 1:6 molar ratio, at 60 °C was accomplished. The uniformly distributed active CaO on the catalyst's surface that drastically improved its basic strength was the origin of the high catalytic activity. Additionally, the negligible drop in activity after the fifth reaction cycle proved the catalyst's stability and was credited

to the integration and stabilization of the active CaO on the FA-ZM support.

Another study reported the preparation of a carbon-based catalyst by the pyrolysis of flamboyant pods followed by functionalization and activation with potassium hydroxide, citric acid, tartaric acid, sulfuric acid, and calcium nitrate to modify either its acidic or basic sites. The catalysts were employed in the methanolysis of safflower oil. Due to its highest specific surface area and potassium and calcium moieties contents, as confirmed by BET and XRD analyses, the alkaline catalyst prepared with potassium hydroxide and calcium nitrate achieved the highest FAME yield of 95% under the following reaction conditions; 5wt% of the catalyst, methanol to oil ratio of 15:1, at 60 °C, for 5h, at a stirring rate of 600 rpm. The catalyst also possessed enhanced stability with 62.2% biodiesel yield after the fourth reaction cycle [7].

Table 6: Summary of base supported alumina catalysts

Catalyst	Optimum yield (%)	Reference
CaO-doped KF (from eggshells)	94.2	[99]
CaO Nanocatalyst (from eggshells)	94	[100]
Calcine walnut shell	98	[101]
CaO/FA-ZM (from eggshells and lignite coal fly)	97.8	[102]
Activated carbon-based catalyst	95	[7]
Mixed CeO_2 (from rare earth hydroxide)	90.42	[34]

Another study reported the synthesis of mixed CeO_2 catalysts utilizing mixed rare earth hydroxide obtained from Thai monazite mineral concentrate as a precursor by co-precipitation method. The performance of these catalysts was optimized in the presence of 10 wt% oleic acids via simultaneous esterification and transesterification of palm oil to biodiesel with 3 wt% of catalyst, 1: 20 oil: methanol molar ratio, at 200 ºC, for 3 hrs., and 600 rpm stirring speed. The XRF results revealed that CeO_2 ranging between 50–67 wt% was the main component of all the synthesized catalysts, with various amounts of Nd, Y, Sm, Pr, Gd, Er, Dy, and La. The effect of varying temperature, stirring speed, and pH of the precipitation was studied to tune the physico-chemical properties of catalysts. Catalyst synthesized at pH 9 and 30 ºC reaction temperature under 400 rpm stirring speed was with the highest surface area of 177 m^2/g and possessed a pore volume of 0.19 cm^3/g with small particle size. It was composed of small-large irregular crystallites accumulating together depicting surface roughness. The study concluded that the surface roughness was the reason for the large specific surface area of the

catalysts which in turn exposed active sites, leading to an increase in the number of catalytic sites accessible for reaction. Indeed, this catalyst gave the highest FAME yield of 90.42%. The work attributed the high FAME yield to the large surface area of the catalyst, the significantly larger amount of Ce and La contents in the catalyst, and the appropriate amount of acid and basic sites on the catalyst [34]. Table 6 summarizes the preparation of waste-derived heterogeneous catalysts and their efficiencies in biodiesel production.

8. CONCLUSION

The review has focused on different heterogeneous catalysts used in transesterification reactions. Additionally, the yields/conversions from these catalysts were examined. Finally, the various conditions necessary for the optimum yield of biodiesel have also been explored. Single and mixed metal oxide catalysts commonly used in transesterification reactions suffered from low activity and stability. Thus, they are modifikingkamkikied by supporting alkaline and alkaline earth metals to improve the active species for efficient biodiesel production. The review highlighted that the modification should be done in such a manner that the supports hold the catalytic species firmly to achieve good reusability.

The review also hinted that owing to its exceptional stability and outstanding textural properties, alumina is an excellent catalyst in many industries. Conversely, alumina was reported to have low activity in transesterification reactions, hence, it has been mostly used as catalyst support. The survey further discovered that the majority of the literature employed commercially available alumina as catalyst support. This alumina suffered from low surface areas which resulted in lower catalytic activity. Thus, the use of Nano-sized alumina as catalyst support with high surface area and enhanced structural properties was recommended. Finally, the review explored solid catalysts prepared from waste materials, all to suggest ways of reducing the overall biodiesel production cost.

9. CURRENT STATUS, FUTURE CHALLENGES AND PROSPECTS

Although solid acid catalysts are efficient in producing biodiesel from feedstocks with high FFA contents, however, in addition to them having slow reaction rate, understanding the parameters controlling solid acid catalyst activity is still vague. This necessitate the introduction of solid basic catalysts, which helps in ensuring biodiesel prominence. Notwithstanding, recent environmental and socio-economical challenges have brought about new demands which require novel catalysts. It should be noted that, one key challenge in designing such catalysts is achieving phase-homogeneous solids with

uniform morphological and chemical properties. Consequently, the design of catalyst is focusing on that.

Furthermore, the current design of catalysts based on the nanomaterials approach offers new tools for chemical process integration at the nanoscale level. Nano-catalysis guarantees the design of chemical plants that can achieve better integration of units to conserve energy and raw materials. This sustainable process offers optimized direct chemical transformation of raw materials into desired products. In addition to minimizing energy consumptions, waste generation, and environmental hazards, utilization of Nano-catalysis also improved process safety, which are the key principles in the Green Chemistry and Engineering approach.

Future advances should lead to the design of novel catalysts that take advantage of self-assembly of catalytic sites in predetermined two- and three-dimensional configurations. Forthcoming researches should also bridge the different catalysis areas: bio-catalysis, homogeneous and heterogeneous catalysis, together by combining the high selectivity of homogeneous cluster catalysts with the stability and versatility of supported heterogeneous catalysts, which in some cases has already shown its potential. Lastly, chemo-enzymatic new reaction routes will have a great impact on chemical manufacturing in the future.

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