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A review on the use of non-conventional heterogeneous catalysts for biodiesel synthesis

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The focus of this review is on the use of non-conventional heterogeneous catalysts for biodiesel synthesis. The review is based on published works that have utilized these non-conventional catalysts for biodiesel synthesis with very good biodiesel yield. The non-conventional catalysts under consideration in this review are those obtained majorly from egg shells. These materials are generally waste materials which several publications had reported to contain high content of calcium oxide. Utilization of these waste materials as catalysts reduces catalyst cost, promotes environmentally benign process and serves as source of income if biodiesel is to be commercialized. Results reported 80 to 90% yield of biodiesel using some of these non-conventional catalysts.

**Key words:** Biodiesel, seed oils, egg shells.

INTRODUCTION

Biofuels have become one of the major solutions to issues of sustainable development, energy security and a reduction of greenhouse gas emissions (Sylvester et al., 2013). Biodiesel, an environmental friendly diesel fuel similar to petro-diesel in combustion properties, has received considerable attention in the recent past worldwide. Biodiesel is a methyl or ethyl ester made from renewable biological resources such as vegetable oils (both edible and nonedible), recycled waste vegetable oil and animal fats (Wilson, 2010). The use of vegetable oils as alternative fuels has been in existence long ago but was set aside due to the availability of petroleum products which appears to be cheaper.

Biodiesel is now recognized as an alternative because it has several advantages over conventional diesel (Aworanti et al., 2013). It is safe, renewable and non-toxic (ca. 98% biodegrades in just a few weeks). It contains less sulphur compounds and has a high flash point (>130°C). It is almost neutral with regards to carbon dioxide emissions, and emits 80% fewer hydrocarbons and ~50% less particles. It enjoys a positive social impact, by enhancing rural revitalization (Anton et al., 2005). It is the only alternative fuel currently available that has an overall positive life cycle energy balance, it yields as much as 3.2 units of fuel product energy for every unit of fossil energy consumed in its life cycle, compared to

Table 1. Showing the various emissions from different blends.

Emission type	B20 (%)	B100 (%)
Total unburned hydrocarbons	20	67
CO	12	48
CO_2	16	79
Particulate matter	12	47
SO_X	20	100
Polycyclic aromatic hydrocarbons(PAHs)	13	80
Nitrated PAHs	50	90

Source: Anton et al. (2005).
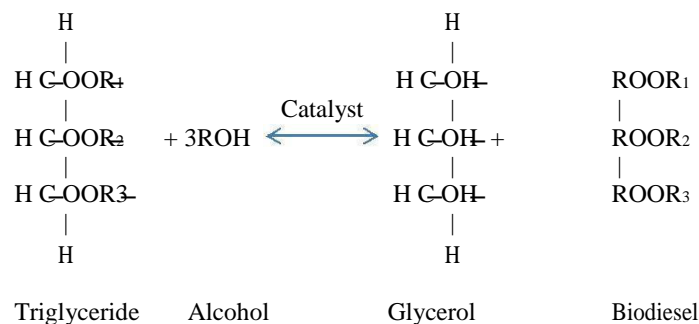
Figure 1. Transesterification of oil with methanol.

only 0.83 units for petroleum diesel (Sheehan et al., 1998). Biodiesel contains no petroleum products, but it may be blended with conventional diesel. A blend of 80% petroleum diesel and 20% biodiesel (known as B20) can be used in unmodified diesel engines. Biodiesel can also be used in its pure form (B100), but this requires minor engine modifications to avoid maintenance problems. Table 1 shows the various emissions from the various biodiesel blends.

Biodiesel is produced by transesterification reaction of triglycerides using alcohol in the presence of a catalyst. Transesterification or alcoholysis, is a reaction in which a fat or oil reacts with an alcohol by using a catalyst to form esters and glycerol (Figure 1). Many types of alcohol can be used such as methanol, ethanol, propanol and butanol.

In the transesterification process, biodiesel is usually prepared in the presence of homogeneous base or acid catalysts. The acid-catalyzed process often uses acid as a catalyst. However, a high molar ratio of methanol to oil is needed; the reaction time is very long and is more corrosive. So, the base catalysts are preferred to be used instead of the acid catalysts because the catalytic activity of a base is higher than that of an acid. In this conventional homogeneous method, the removal of these catalysts is very difficult, and a large amount of wastewater is produced to separate and clean the catalyst and the products. Therefore, conventional

homogeneous catalysts are expected to be replaced by environmentally friendly heterogeneous catalysts. The replacement of homogeneous catalysts by heterogeneous catalysts would have various advantages such as the ease of catalyst separation from the reaction mixture, product purification, and the reduction of environment pollutants (Liu et al., 2008; Shimada et al., 2002; Kulkami et al., 2006; Di Serio et al., 2007; Kawashima et al., 2009). The biodiesel obtained must meet the ASTM standard (Table 2).

Several journals have been reported on the synthesis of biodiesel from conventional catalysts using edible and non-edible seed oils while few has been reported on biodiesel production from same feedstock using non-conventional catalysts. This paper therefore aims at reviewing several publications on non-conventional catalysts with the sole aim of promoting its use as catalyst during biodiesel production (both in commercial and laboratory scale).

Biodiesel feedstock

Biodiesel is an aspect of oil that enhances waste to wealth research. The source of feedstock today for biodiesel production ranges from edible to non-edible vegetable oil, animal fats, algae and waste edible vegetable oil. The production of biodiesel from edible oils

Table 2. Shows American Society for Testing and Materials (ASTM) standards of maximum allowed quantities in diesel and biodiesel.

Property	Diesel	Biodiesel
Standard	ASTM D975	ASTM D6751
Composition	HCa (C_{10}-C_{21})	FAMEb (C_{12}-C_{22})
Kin.viscosity (mm^2/s) at 40°C	1.9-4.1	1.9-6.0
Boiling point (°C)	188-343	182-338
Flash point (°C)	60-80	100-170
Cloud point (°C)	-15 to 5	-3 to 12
Pour point (°C)	-35 to -15	-15 to 16
Water (vol %)	0.05	0.05
Carbon (wt %)	87	77
Hydrogen (wt %)	13	12
Oxygen (wt %)	0	11
Sulfur (wt %)	0.05	0.05
Cetane number (ignition quality)	40-55	48-60
Stoichiometric air/fuel ratio (AFR)	15	13.8
HFRRc (Dm)	685	314
BOCLEd scuff (g)	3600	>7000
Life-cycle energy balance (energy units Produced per unit energy consumed)	0.83/1	3.2/1

a. Hydrocarbons. b. Fatty acid methyl esters. c. High frequency reciprocating rig. d. Ball-on-cylinder lubricity evaluator. Source: Kaewta Suwannakarn (2008.

Table 3. Examples of fatty acid compositions in the oil sources.

Soybean oil from	Cottonseed oil from
Palmitic (C16:0) 11.0%	Palmitic (C16:0) 23.0%
Stearic (C18:0) 4.0%	Palmitoleic (C16:1) 0.9%
Oleic (C18:1) 23.0%	Stearic (C18:0) 2.3%
Linoleic (C18:2) 54.0%	Oleic (C18:1) 16.8%
Linolenic (C18:3) 8.0%	Linoleic (C18:2) 0.1%
Linolenic (C18:3) 0.2%	Others 0.8%

Numbers in parentheses (Cxx:y) signify the number of carbon atoms (xx) and the unsaturated centers (y). Source: Dae-Won Lee et al. (2009).

will increase the price of such commodities in the market and hence create more problems than it has solved for the common man. Hence biodiesel production from non-edible feedstock will serve better in the developing countries. In chemical terms, each feedstock has a specific composition of fatty acids. This is shown in Table 3 for soya been oil (edible) and cotton seed oil (non-edible) (Hoydonckx et al., 2004; Kansedo et al., 2008; Barakos et al., 2008).

The chemical features of fatty acid are collectively described by the carbon number and degree of unsaturation. These features affect the reactivity toward transesterification and, as a result, the properties of the produced biodiesel (alkyl ester). For instance, the fuel properties for biodiesels, such as cetane number, heat of combustion, melting point and viscosity, increase with increasing carbon number and unsaturation degree (Pinto et al., 2005). Due to the variations in the fats obtained from the individual feedstock, the properties of biodiesel may be improved by genetically improving the quality of triglyceride (Dae-Won et al., 2009; Bankovic-Ili et al., 2008; Ivana et al., 2012)).

Some of the non-edible seed oils that have been reported include *Jathropha curcas (*Omotoso et al.,, 2011)*, Mangifera indica* (Idusuyi et al., 2012), *neem, Ricinum communis* and *Gossipium grattima* (Ibrahim, 2013). Some of the non -edible seed oils that are yet to be reported are *Therelia peruviara, Afcola mellanii, Chrisophylum albidum* and *Spondia mombis, Crotalaria spectabilis, cynanchum* leave (honeyvine)*, Fatoua villosa,*

Table 4. Oil content in the seeds of some non-edible plants.

Botanical name	Local name	Oil content (%)
Jathropha curcas	Jathropha	20-60
Ponganta piñnata	Karanja	25-50
Madhuca indica	Mahua	35-50
Schietchera triguga	Kusum	10.65
Azadtrachta indica	Neem	20-30
Ricinum communis	Castor	45-50
Linum usitattsstmum	Linseed	35-45
Cerbera Mangas	Sea Mango	54
Gossypium Spp	Cotton	17-25
Nicotiana tabaccum	Tobacco	36-41
Argemone mexicana	Mexican prickly	22-36
Hevea brasilient	Puppy	40-60
Melta Azedarach	Rubber tree	10
Simmondsta chiments	Persian lilac	45-55
Theretta peruviana	Jojoba	8.41
Moringa oefera	Yellow Oleander	33-41
Thlaspi arvense	Moringa	20-36
Euphorbia lathyrts	Field Pennycress	48
Saptum sebtferum		12-29
Pistacta chinensts		30
Datura stramontum		10.3-23.2

(Source: Bankovic Ilic et al., 2012).

Fumaria officinalis, Phoradendron serotinum, and *Senecio glabellus* (Sylvester et al., 2013). Many of these seeds are wastes in the environment and are rich source of oils (Table 4). If necessary genetic modifications (s) are done on them, they can successfully be a constant source of feedstock for biodiesel production. This is because they are annually produced and are cheap to get, mostly in the developing nations (Taufiq-Yap et al., 2011).

Babagana et al. (2011) reported that the oil yield from seeds of *Balanite aegyptiaca* was 34.52%, the three fatty acids in the extracted oil were mainly identified as; palmitic acid, linoliec acid and stearic acid with 14.73, 75.86 and 9.40% respectively. The yield of the biodiesel after 12 to 24 h reaction was 90%. The oil exhibited good physical and chemical properties which can be used in biodiesel production as the fuel properties were within ASTM 6751 (Table 2) standard specifications. Wilson (2010) reported that the proximate analysis of Jatropha seeds showed the percentage of crude protein, crude fat and moisture were 24.60, 47.25 and 5.54% respectively. Jatropha contains 30 to 40% oil that can be easily expressed for processing (transesterification) and refinement to produce biodiesel. *J. curcas* gives higher oil yield per hectare than peanuts, sunflower, soya, maize or cotton when grown under optimum conditions. The processed oil can be used directly in diesel engines after minor modifications or after blending with conventional diesel. Jathropha has varieties of species and the different species have different oil constituents. Jathropha was known to originate from Mexico. Figure 2 (shaded portions) shows where *Jathropha* species are planted across the globe. The ability of the plant to thrive in Africa and Asia has made it another divine endowment in case our oil goes into extinction (Heller, 1996). Figure 2 shows where Jathropha is found across the globe via the shaded portions.

Results from Akpan et al. (2011) showed that the percentage oil content of castor seed was found to be 33.2% of the total weight of 155.30 g. Castor oil is known to be one of the few naturally occurring glycerides that approach being a pure compound since the fatty acid portion is nearly nine-tenths ricinoleic. It is an annual plant and grows everywhere. Hence castor oil can be a viable source of feedstock for biodiesel production. Sam et al. (2008) reported that *Irvingia gabonensis, Arachis hypogea* and Mustard seed (*Brassica compestus)* contains 51.3, 46 and (35%) oil respectively. These oils can serve as sources of biodiesel if modified in the respective indigenous nations. The lipids of *Persea americana* and *Chrysophyllum albidum* seeds although contain limited amount of oil, they can still serve as supplement oils since they contain high amount of oleic and palmitic acid (Sam et al., 2008). Animal fats and

Figure 2. Jathropha is found across the globe via the shaded portions.
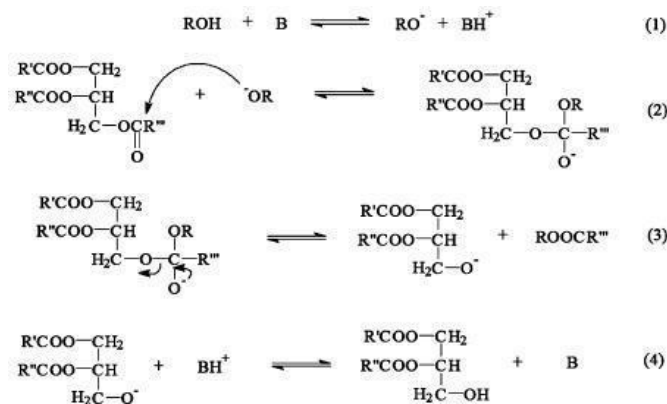

Figure 3. Mechanism for the base catalyzed transesterification reaction.

used edible vegetable oils can as well be modified to become resourceful feedstock for biodiesel synthesis. Ngamcharussrivichai et al. (2008) confirmed that Luffa *cylindrica* seed oil is another possible candidate for biodiesel feed-stock. This is a waste that grows in abandoned places on the street of Africa, Asia and other places in the world. There are several seeds with no use (Table 4) that contains high amount of oil and could satiate the world"s oil need if well managed.

Non-conventional heterogeneous catalysts for biodiesel production

Catalyst is a fundamental requirement for biodiesel production, the choice of catalyst has always resulted into certain level of differences in the course of producing

methyl esters (biodiesel). The catalyst use for biodiesel production is classified into conventional and non-conventional catalysts. Conventional catalysts include base, acid and heterogeneous catalysts. Basic catalysts

such as NaOH, KOH, NaOCH$_3$ and KOCH$_3$ have been employed and reported (Singh et al., 2006). They are the most common, their process is faster and the reaction conditions can be moderated (Reid, 1911; Freedman et al., 1984). However, their utilization in vegetable oil transesterification produces soaps by neutralizing the free fatty acid in the oil and triglyceride saponification. Soap formations here are undesirable side-reactions, because they partially consume the catalyst, decrease the biodiesel yield and complicate the separation and purification steps.

The reaction mechanism (Figure 3) of base-catalyzed transesterification is summarized as follows: The first
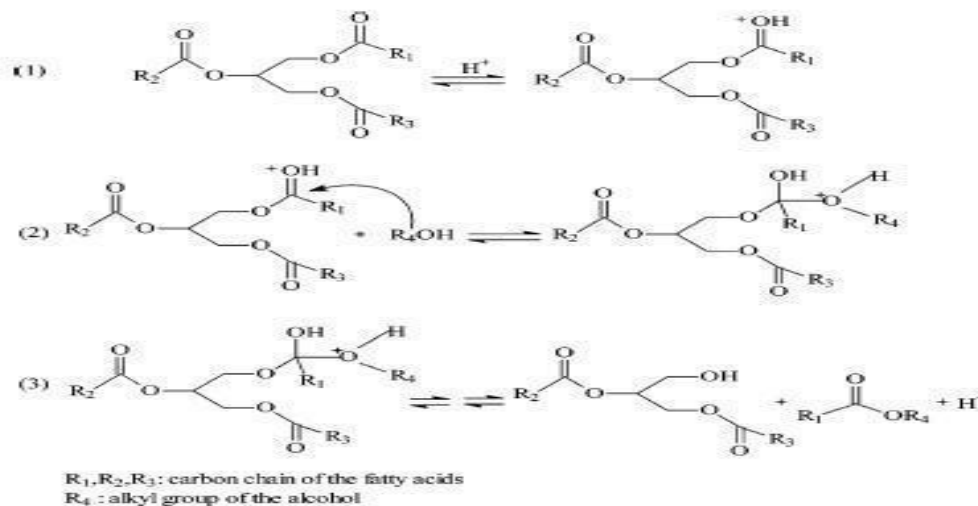
R_1, R_2, R_3: carbon chain of the fatty acids
R_4: alkyl group of the alcohol

Figure 4. Mechanism of the Homogeneous acid-catalyzed reaction.

step is the generation of an alkoxide ion (RO-) through proton abstraction from alcohol by base catalyst (B). Then the alkoxide ion attacks a carbonyl carbon of triglyceride molecule and forms a tetrahedral intermediate ion (step 2), which is rearranged to generate a diglyceride ion and alkyl ester molecule (step 3). Finally, the diglyceride ion reacts with the protonated base catalyst, which generates a diglyceride molecule and turns the base catalyst into the initial form (step 4). The resulting diglyceride is ready to react with another alcohol molecule, thereby starting the next catalytic cycle (Meher et al., 2006; Lotero et al., 2006; Balat and Balat, 2008; Di Serio et al., 2008). For acid-catalyzed reactions (Figure 4), sulfuric acid has been the most investigated catalyst.

Other acids, such as HCl, BF3, H3PO4, and organic sulfonic acids, have also been used by different researchers (Ibrahim, 2013). This process of strong acid catalyzed transesterification reaction can simply be described as the protonated carbonyl group nucleophilicly attacks the alcohol, forming a tetrahedral intermediate; the proton then migrates, and the intermediate decomposes forming a new ester (Lotero et al., 2006).

Homogeneous catalysts are generally limited to batch-mode processing (Jothiramalingam and Wang, 2009). Other steps in the biodiesel production process are time consuming and involve costly processing. These steps are oil pretreatment, catalytic transesterification, separation of fatty acid/methyl ester (FAME) from crude glycerin, neutralization of waste homogeneous catalyst, distillation of accessory methanol, water washing of the FAME phase, and vacuum drying of the desired products (Bournay et al., 2005). Difficulties with using homogeneous catalysts center on their sensitivity to free fatty acid (FFA) and water in the source oil. FFAs react with basic catalysts (NaOH, KOH) to form soaps when the FFA and water content are above 0.50 and 0.06%,

respectively (Ma and Hanna 1999). This soap formation complicates the glycerol separation, and reduces the FAME yield. Each of these steps constitute additional processing time and cost. An example is the separation of the products from the spent waste catalyst which requires a post treatment with large volumes of water to neutralize the used catalyst in the product mixture. This creates an additional process burden by generating waste water that must be treated before release into the environment (Bournay et al., 2005).

Water in the feedstock results in the hydrolysis of FAME in the presence of strong basic or acidic catalyst. Thus, some inexpensive oils, such as crude vegetable oils, waste cooking oil, and animal fats, which generally contain a high content of FFA and water, cannot be directly utilized in existing biodiesel facilities with homogeneous catalysts (Canakci and Gerpen, 1999; Johnston and Holloway, 2007). With all these difficulties, biofuel may never be able to replace petroleum diesel in terms of stress and cost implications (Freedman et al., 1986). This led to the current solution known as second generation technology based on heterogeneous catalysts that are capable of effectively processing less costly feedstocks high in FFAs and water content with a simpler less costly processing method (Figure 5).

Heterogeneous catalysis

Heterogeneous catalysts are promising for the transesterification reaction of vegetable oils to produce methyl esters (biodiesel) and have been studied intensively over the last decade. Unlike the homogeneous catalysts, heterogeneous catalysts can be easily separated from reaction mixture and reused for many times. The major difficulty with heterogeneously
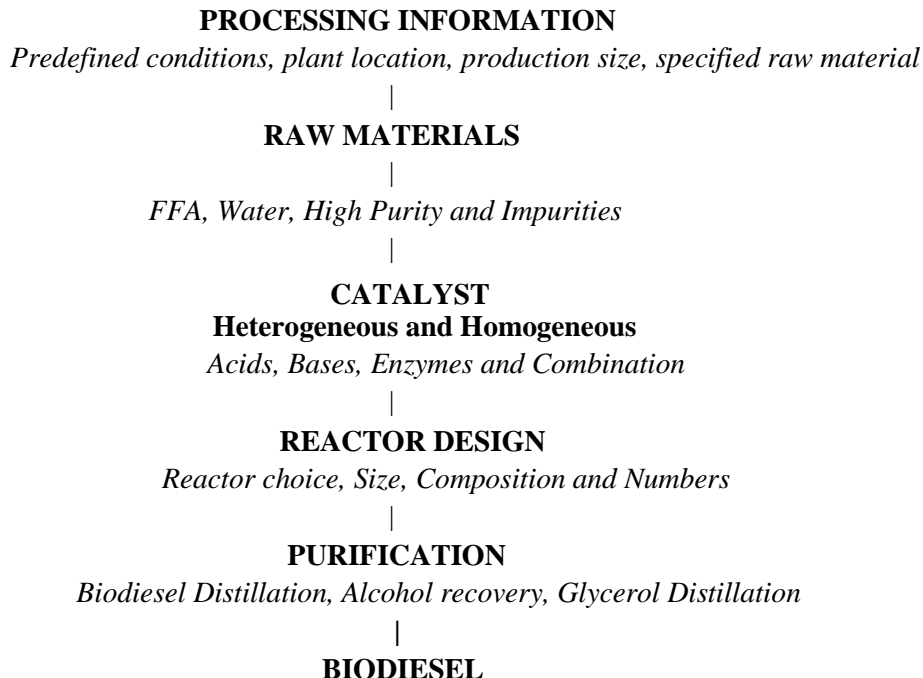
PROCESSING INFORMATION
Predefined conditions, plant location, production size, specified raw material
|
RAW MATERIALS
|
FFA, Water, High Purity and Impurities
|
CATALYST
Heterogeneous and Homogeneous
Acids, Bases, Enzymes and Combination
|
REACTOR DESIGN
Reactor choice, Size, Composition and Numbers
|
PURIFICATION
Biodiesel Distillation, Alcohol recovery, Glycerol Distillation
|
BIODIESEL

Figure 5. Flow diagram for biodiesel production. Source: Sotoft et al. (2010).

catalyzed process is its slow reaction rate compared with the homogeneous process. To overcome this major challenge, the reaction conditions of heterogeneous catalysis are intensified by increasing reaction temperature (100 to 250°C), catalyst amount (3 to 10 w%) and methanol/ oil molar ratio (10:1 to 25:1) (Jutika et al., 2011: Shuli et al., 2010).

Another problem of the heterogeneous process is the dissolutions of active species into liquids, which makes the catalysis partly „homogeneous" and then causes problems in biodiesel quality and limits the repeated utilization of catalyst (Dae-Won et al., 2009). Many studies about the use of heterogeneous catalysts for transesterification treated anti-leaching performance as issue of equal importance to catalytic activities. The deactivation mechanism of heterogeneous catalysts towards transesterification can be classified into the leaching of active species and the adsorption of acidic hydrocarbons onto basic sites (Heydarzey et al., 2010).

The deactivation tests usually take the form of repeating the reaction cycle several times and measuring the catalytic activity in the interval between each cycle. If the deactivation of the catalyst is unavoidable, a method for regenerating is welcome. They are environmentally benign and could be easily operated in continuous processes (Dae-Won et al., 2009). This review classifies the solid catalysts into two categories based on their mode of production, that is, the conventional heterogeneous catalyst and non-conventional heterogeneous catalysts.

Conventional heterogeneous catalysts

The conventional catalysts are chemically synthesized catalysts. They are the heterogeneous solid base catalysts" and the heterogeneous solid acid catalysts. The classification of heterogeneous base catalysts is shown in the Table 5.

The history of heterogeneous base catalysis is shorter than that of heterogeneous acid catalysis. Although well-known acidic materials also possess basic characters, base catalyzes by solid materials were not utilized in the early developmental period, because the basic sites are easily covered with atmospheric components such as

CO_2, H_2O, and O_2, which generate carbonate, hydroxide and peroxide, respectively, and incapacitate the function of the basic sites. It was not recognized until the early 1970s that the basic sites could be resurfaced with thermal pretreatment at over 725 K, which removed the poisonous coverings (Hattori, 2004). Studies on solid base catalysts began burgeoning in the 1970s. The mechanism for heterogeneous basic catalyst is similar to that of base catalyst (Figure 5). Several researches have been reported using basic heterogeneous catalysts with good biodiesel yield.

Bancquart compared the base-catalyzed activities of single metal oxides, La_2O_3, MgO, CaO, and ZnO, for the transesterification of glycerol with fatty acid methyl esters (FAME) at 220°C. He concluded that the reaction rates by single metal oxides directly depend on the basicity of the oxide, especially of the strong basic sites (Bancquart

Table 5. Classification of heterogeneous base catalysts.

Basic oxide	Classification
Single component metal oxides	Alkali metal oxides, Alkaline earth oxides, Rare Earth metal oxides, ThO_2, ZrO_2, ZnO, TiO_2
Zeolites	Alkali ion-exchanged zeolite, Alkali ion-supported zeolite.
Supported alkali metal	Alkali metal ions on alumina, Alkali metal ions on Silica, Alkali metal on alkaline earth oxides. Alkali Metals and alkali metal hydroxides on alumina
Clay minerals	Hydrotalcites, Crysotile, Sepiolite
Non-oxides	Alkaline alkoxide, Alkaline carbonate Guanidine-containing catalysts
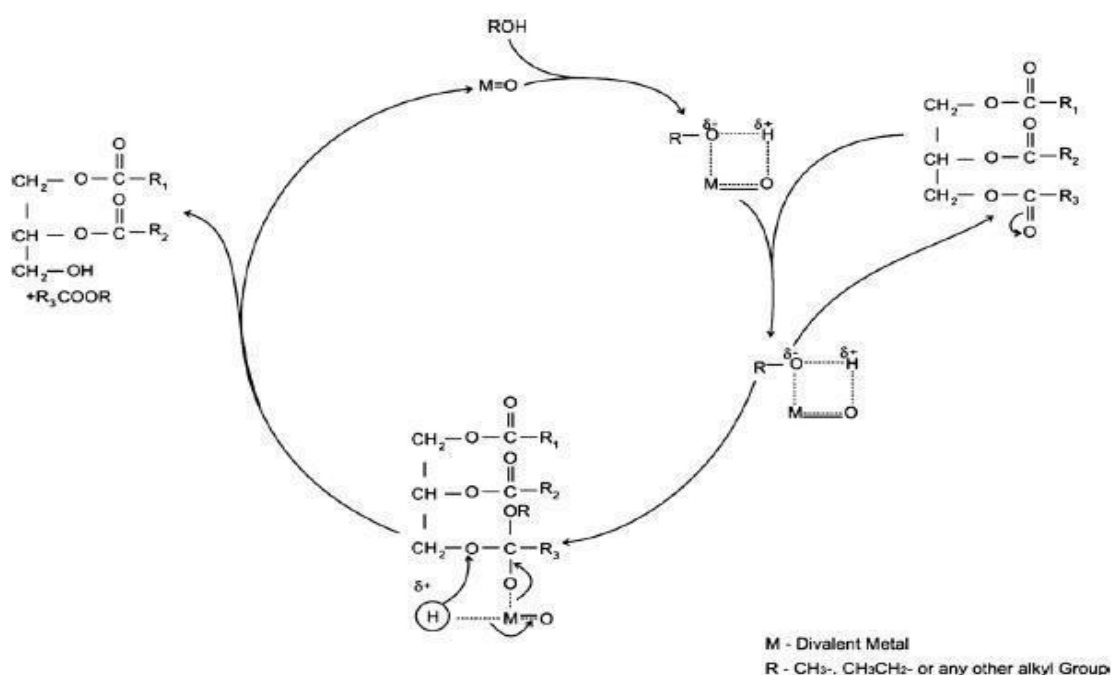
Figure 6. Mechanism of a general base heterogeneous catalyst during transesterification reaction (Dae-Won et al., 2009).

et al., 2001). Therefore, the order of activity followed that of the intrinsic basicity of oxides: La_2O_3<MgO << ZnO = CeO_2.

Babu et al. (2008) investigated the transesterification activities of co-precipitated Mg–La oxides obtained by precipitating both nitrate precursors with KOH/K_2CO_3, which contained MgO, La_2O_3, and La_2MgO_x phases. With increasing magnesium content in the mixed oxides, the basicity of the Mg–La oxides increased but the surface area decreased. The conversion of sunflower oil using Mg–La oxide (Mg/Al = 3 in weight) reached 100% within 2.2 h, even at room temperature, using 5 w% catalyst (b/o oil w) and a methanol/oil molar ratio of 20:1. The activities of the Mg–La oxides were compared with those

of the CaO, SrO, Mg–Al, and Li–Al oxides, which demonstrated the superior activity of the Mg–La oxides. The catalysts showed tolerant activities even in the presence of FFAs and water, which the authors attributed to the super basicity of the catalysts. Several other base solid catalyst have been employed in biodiesel synthesis with good results but were all obtained by conventional mediums (Supamathanon et al., 2011; Qian et al., 2008; Reid, 1911; Rodriguez-Navarro et al., 2010; Sam et al., 2008; Sharma et al., 2010; Sheehan et al., 1998) (Figure 6).

Solid acid catalysts have been studied extensively and used as catalysts or catalyst carriers in the chemical industry, particularly in petroleum for many years. Many
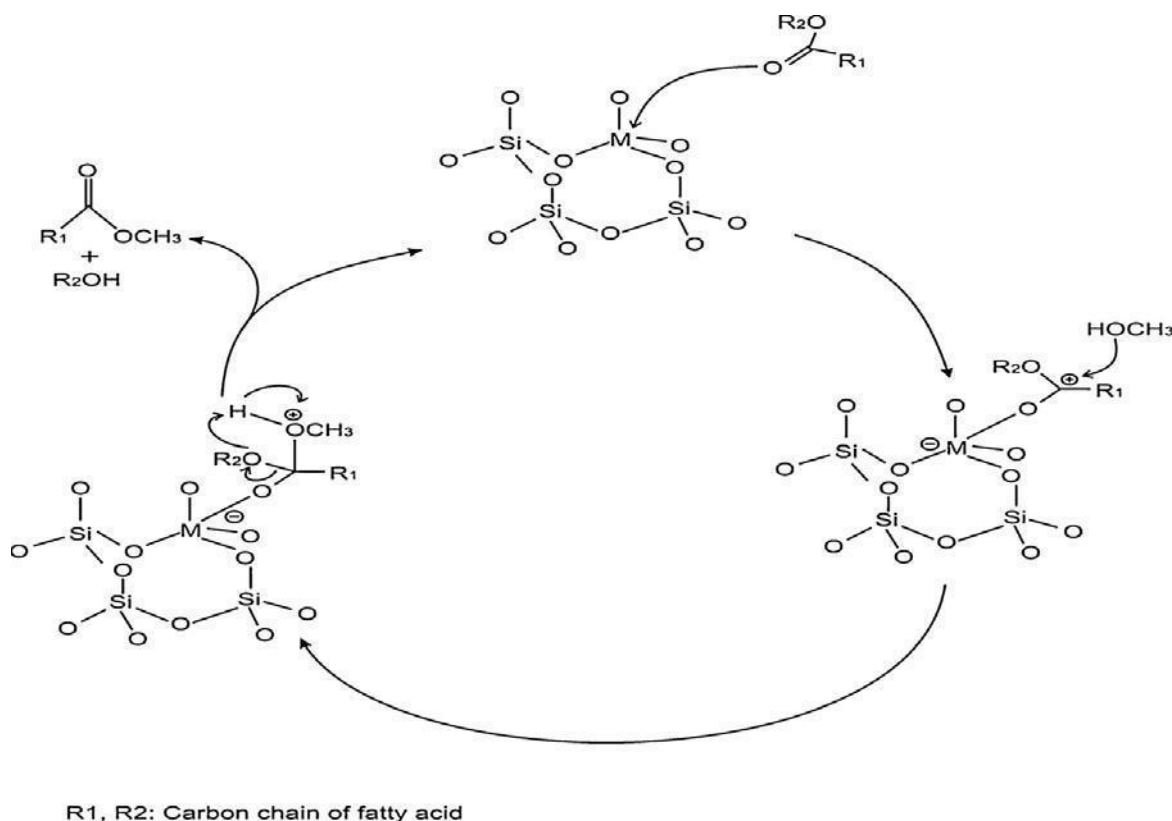
R1, R2: Carbon chain of fatty acid

Figure 7. Showing schematic representation of the chemical mechanism of a heterogeneous acid catalyst (Edger et al., 2010) M, Zr, Hf.

solid acid catalysts have been found and their acid properties on catalytic action and the structure of their acid sites been actively investigated. A solid acid catalyst should possess high stability, numerous strong acid sites, large pores, a hydrophobic surface providing a favorable condition for reaction, and should also be economically viable, insensitive to free fatty acid (FFA) content, esterification and transesterification occurs simultaneously (Dalai and Meher, 2006), eliminate the washing step of biodiesel, easy separation of the catalyst from the reaction medium, resulting in lower product contamination level, easy regeneration and recycling of catalyst and reduction of corrosion problem, even with the presence of acid species (Suarez et al., 2007). The mechanism of acid catalyzed transesterification reaction is illustrated in Figure 7.

Non- conventional catalysts

These are natural or biological materials that can serve as heterogeneous catalysts. This include eggshells; waste shells of mollusk, industrial eggshell wastes, carbonate rocks, oyster shell, crab shells, chicken shells, duck shell, *Turbonilla striatula* shell, quail eggshell,

laterites and lots more (Nakano et al., 2010). Most of these are wastes generated in various nations; they can serve as cheap source of catalysts that are employable in biodiesel production. This will lead to the reduction of cost, waste recycling, and clean environment and enhances waste to wealth.

## Waste shells in biodiesel production

Eggshells

Eggshell is a bioceramic composite which consists of a mineral part containing 95% calcite aggregates pervaded with an organic matrix resulting in a structure which has excellent mechanical properties (Rodriguez-Navarro et al., 2010). The chicken eggshell comprises calcified shell and shell membranes including inner and outer membranes. Further investigations on chicken eggshell have revealed that the chicken eggshells are mainly composed of calcium carbonate along with some traces of magnesium carbonate, phosphate, sodium, potassium, carbon, zinc, manganese, iron and copper. In the elemental composition of eggshell, it has been reported that the major element is calcium and its amount is about

98.2% in the shell. The other elemental compositions are 0.9% magnesium and 0.9% phosphorus (present in shell as phosphate).

Preparation and application of eggshells as catalysts for transesterification reactions

Eggshells can be collected from anywhere. To remove the edible portion attached to the eggshells and other impurities, eggshells should be rinsed thoroughly with tap water until the organic matter, which adheres on the inner surface of the eggshells, is removed, followed by double rinsing with distilled water. The washed eggshells were dried in a hot air oven at 105°C for 24 h. The dried eggshells should be grounded in an agate mortar until they became a powder form. Thereafter, the ground eggshells should be calcined in an open furnace at 900°C. The characterizations is done using X-ray diffraction (XRD), differential thermal analysis/thermogravimetric analysis (DTA/TGA), and Fourier transform infrared (FTIR) spectroscopy experiments on the raw and calcined eggshells. The peaks obtained from XRD and FTIR is noticed. If there are prominent peaks indicating the presence of calcium oxide, then it is applied as catalyst following the regular biodiesel production methodology (Sharma et al., 2010).

Release of CO_2 confirms the formation of calcium oxide, which acts as a catalyst in biodiesel synthesis. Release of CO_2 confirms the formation of calcium oxide, which acts as a catalyst in biodiesel synthesis.

$$CaCO_3 \longrightarrow CaO + CO_2$$
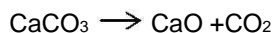
Countries like Japan and South Korea have lots of oyster. The oyster shells are the unwanted waste product from mariculture and present a major disposal problem. This waste generated has affected the environment and the ecosystem resources (Khemthong et al., 2011). It produces nasty smell as a consequence of the decay of flesh remnant attached to oyster or the microbial

decomposition of salts into gases such as NH_3, H_2S and Amine. Therefore conversion of the waste oyster shells to a beneficial and economically viable product can solve the problem partially, if not fully. Kwon et al. (2004) used the waste oyster shells as an effective reagent for phosphorous removal from waste waters. They found that the shells contained mainly calcium carbonate but when it was heated at higher temperatures of 750 to 800°C, it was converted to calcium oxide. CaO formation was confirmed by XRD patterns obtained from the study.

In another experiment, Chae et al. (2006) recycled the oyster waste shells by treating it with plasma pyrolysis technique. These experiments showed that the oyster shells were mainly composed of $CaCO_3$ but when heated to certain temperatures lead to the formation of single metal oxide-CaO. This conclusion helped Nakatani et al.

(2009) to employ combusted oyster shell for transesterification. They combusted the waste oyster shells at different temperatures of 100, 500, 700, 800, 900 and 1000°C for 3 h and discovered that the XRD patterns obtained for the combusted oyster shells at 700°C and above were identical to those of CaO. They applied factorial design and response surface methodology to optimize the reaction conditions. It was observed that the most important factor affecting the biodiesel purity was the reaction time and catalyst concentration. From a second order model, the optimum reaction conditions of catalyst concentration and reaction time was found to be 25 w% and 5 h, respectively. They claimed that the oyster shell combusted at higher temperatures could be reused as catalyst for biodiesel production and the yield obtained was comparable to that of CaO. Boro et al. (2011) investigated the performance of *Turbonilla striatula* shells as catalyst in the transesterification of mustard oil. They observed that catalyst calcination temperature is the most important factor affecting the transesterification process. They reported that the catalyst calcined above 800°C showed better catalytic activity than those calcined at lower temperature. This was attributed to the formation of CaO at higher calcination temperature. The catalyst was deactivated after repeated use and its initial catalytic activity could be regained by calcining the recovered catalyst at 800°C.

Boey et al. (2009) investigated the use of waste shells of mud crab as catalyst with 97% yield. Reusability studies for the same catalyst showed a drop in catalytic activity which was attributed to the loss of active sites due to covering by the resultant. The catalyst has an advantage that it could be regenerated by treating it in soxhlet"s apparatus with petroleum ether as solvent for 3 h. In a similar experiment carried out by Sharma et al. (2010), used recycled chicken eggshells after calcination as catalyst for biodiesel synthesis from karanja oil from the pongam tree (*Pongamia pinnata*).

The catalyst was characterized on X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and differential thermal analysis/thermogravimetric analysis (DTA/TGA). The formation of the calcium oxide phase was confirmed at 900°C after calcination. A high biodiesel yield of 95.0% and conversion of 97.4% was obtained at an 8:1 (alcohol/oil) molar ratio, 2.5 w% catalyst, and 2.5 h reaction time at 65± 0.5 C.

The biodiesel conversion was determined by Fourier transform nuclear magnetic resonance (FTNMR) spectroscopy. Khemthong et al. (2011) derive active biodiesel production catalysts from waste eggshells by simple calcination in air. The physicochemical properties of the activated catalysts were characterized by XRD, N_2 sorption, CO_2-TPD, TGA–DTG, XRF, and SEM, while the catalytic activity was tested in producing biodiesel via transesterification on palm oil with methanol under microwave conditions of varying temperatures. The effect

of microwave power, reaction time, methanol-to-oil ratio, and catalyst loading was investigated. The experimental results revealed that the catalysts exhibited a high content of CaO (99.2 wt%) with a high density of strong base sites. The catalytic testing demonstrated a remarkable enhancement for biodiesel production using microwaves compared to conventional heating. The maximum yield of fatty acid methyl esters reached 96.7% under the optimal condition of reaction time of 4 min with 900 W microwave powers, methanol-to-oil ratio of 18:1, and catalyst loading of 15%. The results indicated that the CaO catalysts derived from eggshells showed good reusability and had high potential to be used as biodiesel production catalysts under microwave-assisted transesterification of palm oil.

Viriya-empikul et al. (2010), utilized waste shell of eggs of golden apple snail, and meretrix venus as catalyst to produce biodiesel from transesterification of palm olein oil. The shell materials were calcined in air at 800°C with optimum time of 2 to 4 h to transform calcium species in the shells into active CaO catalysts. All catalysts showed the high biodiesel production activity over 90% fatty acid methyl ester (FAME) in 2 h, whilst the eggshell-derived catalyst showed comparable activity to the one derived

from commercial $CaCO_3$. The catalytic activity was in accordance with the surface area of and the Ca content in the catalysts.

Conclusion

Transesterification reaction is highly influenced by the reaction conditions, catalyst used, and molar ratio of methanol to oil. The catalyst synthesized with the waste shells gives way for renewable catalyst and at the same time recycles the waste generated. The various shells that have been employed have proved that highly active and reusable solid catalysts can be prepared with no time loss by just calcining the shells. Utilization of these waste materials not only reduces the catalyst cost but also promotes environmentally benign process. These shells may also find their utility in other base catalyzed important organic reactions which will add value to the waste generated. The waste shell catalyst generates calcium oxide essential for adsorption.

The CaO catalysts derived from eggshells possessed mainly the strong base sites with average base site density of 194- $molm^{-2}$ which exhibited an excellent performance in producing biodiesel under microwave conditions. The assistance of microwave irradiation enhanced the rate of transesterification reaction compared to the conventional heating method. The highest biodiesel yield (96.7%FAME) was observed by addition of 15 wt% of the catalyst to a mixture of MeOH/oil via microwave irradiation at 900 W for 4 min. In the process, the CaO catalyst derived from eggshell still maintained the catalytic activity and crystalline phase

after being reused 5 times.

Commercial biodiesel production from waste materials as feedstock and waste shells as catalysts will help to reduce competition of edible products as feedstock, eliminate environmental problems, create more jobs, reduce high cost of biodiesel production and go a long way to reduce global warming. It is with this view that this paper encourages that future researches involving biofuel should consider this aspect of biodiesel to make the production more economically feasible even in the developing world.

Conflict of Interest

The authors have not declared any conflict of interest.

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