Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 7, No. 3, p. 36-49, 2015
http://www.innspub.net

INNSPUB

REVIEW PAPER

OPEN ACCESS

Animal renewable waste resource as catalyst in biodiesel production

A. Gorji

Young Researchers and Elite Club, South Tehran Branch, Islamic Azad University, Tehran, Iran

Article published on September 17, 2015

Key words: Animal waste, Animal bones, Egg shell, Mollusk shell, Biodiesel.

Abstract

Anxieties increased for using fossil fuels and attention of nations to replacing clean fuels such as biodiesel to that due to decreasing of fuel sources and increasing of energy demand and on the other side whether pollution and environmental problems. Using renewable waste resources in producing biodiesel has been considered by researches due to the less environmental pollution and reducing its production cost. Animal bones, mollusk shells and egg shells are among resources of renewable animal waste that have been researched to produce biodiesel as catalyst. This study is a review of researches that carried out. Studies show that catalysts that produced from renewable animal waste can be applied to produce biodiesel because of availability, abundant resources, renewability, efficient catalyst activity, low cost and possibility to reusing of mentioned catalyst.

***Corresponding Author:** A Gorji ✉ m.akbar.gorji@gmail.com

Introduction

Increasing of energy demand in the world and decreasing of fossil fuels in one side and World Health matter in another side are factors emphasize on necessity of reconsideration to use current fossil fuels. Using fossils fuels during past years caused to decreasing of related resources as well as air pollution. The best alternatives to fossil fuels are renewable and clean energies such as solar energy and environmental fuels; biodiesel is the most common environmental fuels (Dias *et al.*, 2008; Guan *et al.*, 2009; Mighani *et al.*, 2009; Mohadesi *et al.*, 2014; Moradi *et al.*, 2015). Biodiesel considered by researchers and nations for its advantages such as better lubrication, non-toxic full oxidation because of having 10-12 oxygen, spreading of low contamination such as Sulfur oxides, mono carbon oxides, biodegradable and decreasing of World Health problems (Atabani *et al.*, 2014; Ghanei, 2014; Mohammadi *et al.*, 2014; Sharma *et al.*, 2014; Shirazi *et al.*, 2014). In 1990, this fuel is the only fuel that approved from clean air movement because of suitable environmental properties (Jacobson *et al.*, 2008).

Biodiesel can be produced from vegetable oils like palm kernel, soybean, hazelnut, castor, tobacco seed, Jatropa, mustard, sunflower and animal fats like waste tallow, sheep fat, fish oil, lard, chicken fat and also waste edible oils like waste frying oils that use of animal fats and waste edible oils as renewable resources can decrease cost of biodiesel production and help to lower environmental pollution (Aladetuyi *et al.*, 2014; Balat and Balat, 2010; Beetul *et al.*, 2014; Gorji and Ghanei, 2014; Menetrez, 2014; Sbihi *et al.*, 2014; Sohpal and Singh, 2014).

.

According to the definition American Society for Testing and Materials (ASTM), biodiesel is "mono alkyl esters of oily acid with long chain that produced from renewable oily raw material such as vegetable oils or animal fat". "Bio" phrase is renewability symbol and its biological origin and "diesel" is similarity to diesel fuel and its application in diesel motor. Meanwhile, biodiesel called "methyl esters oily acid" or "FAME" because methanol is cheaper and more available than ethanol and other alcohol (Demirbas, 2009; Gorji and Ghanei, 2014; Graboaki and McComick, 1998; Nag, 2008).

For producing biodiesel from vegetable oil and animal fats three main ways are applied: pyrolysis, micro emulsions and transesterification; the last one is the most common way (Ghanei *et al.*, 2011). Transesterification produced by oil and alcohol reaction with a suitable catalyst and at the same time glycerin produced as valuable by-product of this process as shown in fig. 1 (Ghanei *et al.*, 2011; Strabuck and Harper, 2009). In this reaction additional methanol applied for leading balance to the right and increasing methyl ester conversion (Demirbas, 2009; Gorji and Ghanei, 2014).

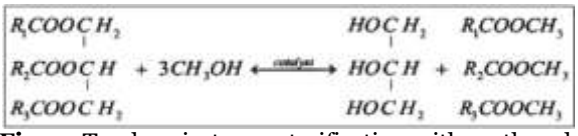

Fig. 1. Tryglycerin transesterification with methanol (Ghanei *et al.*, 2011).

Catalyst in producing biodiesel

Generally, catalysts divided into three categories: homogenous, heterogeneous and enzymes. Till now, many studies have been done regarding to homogenous catalyst. During current years, using homogenous catalyst not qualified by researchers because of multi-step reaction and expensive cost of biodiesel production such as cost of waste processing, products purification and catalyst deactivation, for mentioned reasons using heterogeneous catalysts considered researchers (Borges and Díaz, 2012; Semwal *et al.*, 2011; Simões *et al.*, 2015; Singh Chouhan and Sarma, 2011). Replacing homogenous by heterogeneous catalysts caused to eliminate several separation reaction, corrosion and hazardous waste. One of the most important properties of heterogeneous catalysts is reusing of these catalysts as well as non-formation of soap that caused to less washing and to eliminate possibility of forming emulsion (Kansedo *et al.*, 2009; Kim *et al.*, 2009; Lou

et al., 2008). Carried researches show that heterogeneous catalysts in comparison with homogeneous have less sensitivity to the presence of FFA (Li *et al.*, 2009).

Using enzymatic catalysts is a fully clean and selective process with suitable result. Among the obstacles for these catalysts following matters can be mentioned: long reaction time, expensive costs, lack of recycling and reusing (Balat and Balat, 2010; Dizge *et al.*, 2009; Helwani *et al.*, 2009). In fig. 2 catalyst classification shown (Gorji and Ghanei, 2014).

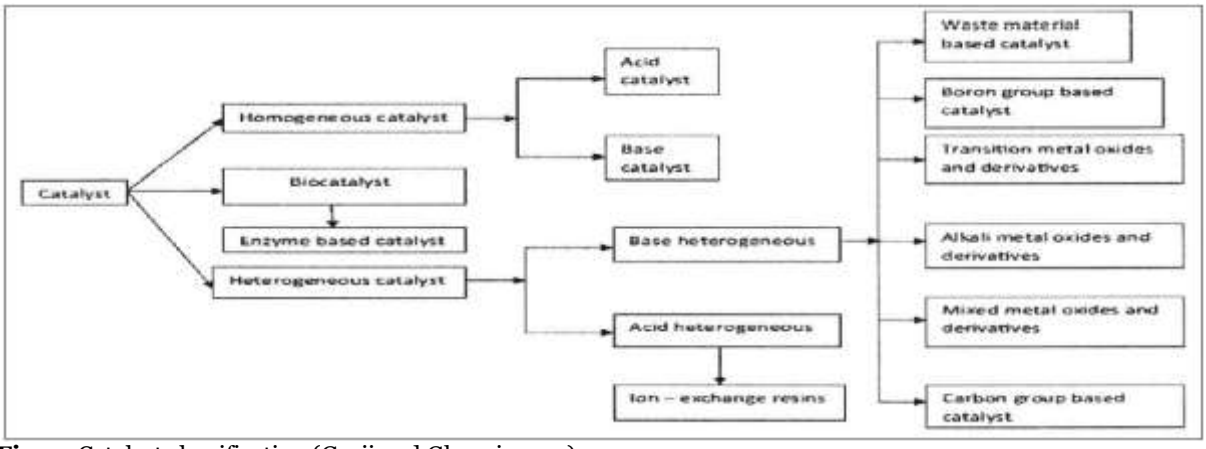

Fig. 2. Catalyst classification (Gorji and Ghanei, 2014).

Renewable animal waste as catalyst

One of the methods of decreasing biodiesel production cost is using of created waste from different occupation to supply feed and catalyst required for reaction, moreover, using waste help to less pollution and increasing of World Health. During past years, several researches done on using renewable animal waste like shell eggs, clams skin and animal bones as catalyst. Researches show that animal waste resources that used as catalyst converted to calcium oxide after calcine (Boey *et al.*, 2011a; Khalili-Darmani *et al.*, 2011, Nurfitri *et al.*, 2013; Suryaputra *et al.*, 2013; Wijaya *et al.*, 2013).

Among heterogeneous catalysts calcium oxide has special place to biodiesel production. In this regard, many essays published (Suryaputra *et al.*, 2013). Researchers for the following reasons have attention to calcium oxide: cheapness, availability, possibility to reusing, having various renewable resources for this catalyst (Suryaputra *et al.*, 2013; Khalili-Darmani *et al.*, 2011).

Table 1 shows the properties and table 2 shows the some of researches of calcium oxide (Boey *et al.*, 2011a).

Table 1. Calcium oxide properties (Boey *et al.*, 2011a).

Item	Description
Chemical name	Calcium oxide
Chemical formula	CaO
Common name	Lime, Calx, Quicklime, Burnt lime, Unslaked lime, Fluxing lime, Caustic lime
Density (g/cm^3)	3.40
Melting point (°C)	2572
Boiling point (°C)	2850
Heat of formation (kcal/mol)	151.9
Heat of hydration (kcal/mol)	15.1
Solubility of $Ca(OH)_2$ (g/100g H_2O)	0.219
Decomposition temperature (°C)	547
Applications	In furnace lining, Metal smelting, Glass making, Fertilizer, Drying agent, Mortar, Paper and pulp production, Drilling fluid, Pollution control, Water purification, Sugar and cellulose industries, Medical (destroys warts, moles)

Table 2. Conducted researches on biodiesel producing from oil seed by using calcium oxide that yielded from renewable resources.

Biodiesel feedstock	Waste sources	Catalyst preparation		Reaction conditions				Conv. (C) or Yield (Y) (%)	Reusability	Ref.
		Calcination temperature (˚C)	Calcination time (h)	MeOH:Oil (mol:mol)	Catalyst (wt.%)	R.T. (˚C)	R.t. (h)			
Egg shell	Soybean oil	1000	2	9:1	3	65	3	Y=95	13	Wei *et al.*, 2009
Egg shell	Rapeseed	900	2	9:1	3	60	3	Y=96	14	Jazie *et al.*, 2013
Egg shell	Waste frying oil	CaO-900-600	2.5 & 3	12:1	5	65	1	C=94.52		Niju *et al.*, 2014
		CaO-900	2.5	12:1	5	65	1	C=79.62		
Chicken Egg shell	Karanja oil	900	2	6:1	2.5	65±5	2.5	C=97.43		Sharma *et al.*, 2010
Chicken Egg shell	Palm oil	800		12:1	1.5	65	2	C=98	5	Cho and Seo, 2010
Quail Egg shell		800		12:1	1.5	65	2	C=98	5	
mussel shell	Soybean oil	1050	2	24:1	12	60	8	Y=94.1	5	Rezaei *et al.*, 2013
freshwater mussel shell	Chinese tallow oil	Not calcinaton		12:1	5	70	1.5	No reaction		Hu *et al.*, 2011
		CaO-900	4	12:1	5	70	1.5	Y=71		
		CaO-900-600	4 & 3	12:1	5	70	1.5	Y=96	7	
combusted oyster	Soybean oil	700	3	6:1	25	65	5	Y=73.8		Nakatani *et al.*, 2009
Shrimp shell	Rapeseed oil	Shrimp shell was incompletely carbonized at 450 ˚C in a muffle furnace, completely dipped in the solution of KF with mass ratio 25 wt% and then activated at 250 ˚C in muffle furnace for 2 h.		9:1	25	65	3	C=89.1		Yang *et al.*, 2009
mud crab shell	Palm oil	700	2	0.5:1 Mass ratio	5	65	2.5	C=95.6	11	Boey *et al.*, 2009
Snail shell	Waste frying oil	900	3.5	6.03:1	2	60	8	C=99.58 Y=87.28		Biral *et al.*, 2012
shell of T. striatula	Palm oil		4	9:1	3	65±5	6	Y=93.3		Boro *et al.*, 2011
cockle shell	Palm olein oil	900	2	0.54:1 Mass ratio	4.9	65	3	Y>97	3	Boey *et al.*, 2011b
Clam shell	Waste frying oil	900	3.5	6.03:1	3	60	3	C>89 Y>97		Nair *et al.*, 2012
Pomacea sp. shell	Palm oil	900	2	7:1	4	60	4	Y=95.61		Margaretha *et al.*, 2012
Biont shell	Rapeseed oil	Biont shell was incompletely carbonized at 500 ˚C in a muffle furnace, completely dipped in the solution of KF with 25 wt% for 6 h and then activated at 300 ˚C in muffle furnace.		9:1	3	70	3	Y=97.5		Xie *et al.*, 2008
Exoskeleton (pila globosa) shell	frying oil	900	2.5	10:1	4	60±0.5	5	C=97.8 Y=92		Agrawal *et al.*, 2012
chicken bones	Cooking oil	800-1000		15:1	5g	65	4	C=89.32	4	Farooq *et al.*, 2015
sheep bones	Palm oil	800		18:1	20	65	4	C=96.78		Obadiah *et al.*, 2012
Egg shell	Palm olein oil	800	4		10	60	2	C=99.21		Viriya-empikul *et al.*,2010
golden apple snail		800	4		10	60	2	C=99.05		
meretrix venus		800	4		10	60	2	C=98.59		
Egg shell	Palm olein oil	800	4	12:1	10	60	2	Y=94.1		Viriya-empikul *et al.*,2012
golden apple snail		800	4	12:1	10	60	2	Y=93.2		
meretrix venus		800	4	12:1	10	60		Y=92.3		
Mussel shell	Palm oil	1000	4	9:1	10	65	3	Y=97.23	4	Buasri *et al.*, 2013
Scallop shell		1000	4	9:1	10	65	3	Y=96.68	4	
Cockle shell		1000	4	9:1	10	65	3	Y=94.47	4	
crab and cockle shells	chicken fat	900	2	0.55/1 Mass ratio	4.9	-	3	C=98		Boey *et al.*, 2011c

R.T = Reaction temperature, R.t= Reaction time, Y= Yield, C= Conversion.

Egg shells

Egg shell is a bioceramic compound included 95% mineral section (calcite) and organic template having good mechanical properties (Boro *et al.*, 2012), mechanical protective function and micro bacterial (Obadiah *et al.*, 2012).

Most of the researches showed that shell eggs are basically consists of calcium carbonate along with little amounts of magnesium carbonate, phosphate, sodium, potassium, carbon, zinc, manganese, iron and copper (Boro *et al.*, 2012).

Using of bird eggs, especially eggs as part of the food chain of human through the world caused to produce large volume of shell eggs daily. Using this waste shell can help to protecting the environment. Conducted researches show using of egg shell as a catalyst in various fields such as lactose production from milk ultrafiltration as a lactose sources (Boro *et al.*, 2012; Montilla *et al.*, 2005), producing dielectric material and zeolite type A (Boro *et al.*, 2012; Tangboriboon *et al.*, 2010b).

Wei *et al.* (2009) evaluated eggshell as a heterogeneous alkaline transesterification reaction of soybean oil with methanol. At first, eggshell washed and dried and were calcined at different temperatures (200-1000 °C). They explained that shell structure had no changes before 600 °C, structure changing started at 700 °C. Moreover, at temperatures above 800 °C particles size became smaller. Using XRD analysis, they showed that at temperatures below 700 °C large amount of calcium carbonate exist in egg shell and by increasing temperature CaO increased as well, so calcinate temperature is effective on conversion.

They reported rate of conversion 95% for optimal ratio of methanol to oil 9:1, 3 wt% calcinated catalyst at 1000 °C, reaction temperature 65 °C and in reaction time of 3 h. Ability to reusing of CaO catalyst evaluated in this study. Results showed that catalyst can be used 13 times without obvious increasing in its activity but by increasing using time activity increased gradually.

That stated that using this cheap and nature-friendly catalyst can effected biodiesel production economically. Jazie *et al.* (2013) in another study reviewed producing biodiesel from rapeseed oil by using egg shell. In this study, egg shells washed and dried at 105 °C for 24 h, then calcined at 200-1000 °C for 2 h.

They reported that at calcinate temperature 900 °C maximum surface area and pore sizes of 59.071 m^2/g and 0.109 Cm^3/g yielded respectively. Besides, reported conversion rate of 96% for optimal ratio of methanol to oil 9:1, catalyst rate 3 wt% (calcined at 900 °C for 2 h), reaction temperature 60 °C and reaction time 3 h.

They mentioned that catalyst can be used 14 times without obvious increasing in its activity but by increasing using time activity increased gradually.

Niju *et al.* (2014) studied on producing biodiesel by using Waste frying oil transesterification reaction by egg shell produced by calcination-hydration-dehydration to prepare calcium oxide with high activity. In this study egg shells washed with distilled water and dried at 115 °C for 24 h, then calcined at 900 °C for 2 h (egg shell-CaO-900). Calcinated catalyst refluxed in 60 °C water for 6 h and re-calcined at 600 °C (egg shell-CaO-900-600).

They evaluated producing biodiesel in reaction condition of methanol to oil 12:1 at temperature 65 °C for 1 h and catalyst rate of 5 wt% for commercial calcium oxide, egg shell-CaO-900 and egg shell-CaO-900-600. In this way for catalyst surface area 3.0022, 3.7262 and 8.6401 m^2/g and conversion rate of 67.57%, 79.62% and 94.52% reported respectively.

In addition, they reported that egg shell-CaO-900-600 catalyst showed the greatest alkaline strength ($12.2<H_-<15$). Table 3 shows the results of this study.

Table 3. Surface area, alkaline strength and conversion rate resulted from various catalysts (Niju *et al.*, 2014).

Conversion rate (%)	Alkaline strength (H)	Surface area (m^2/g)	Catalyst name
67.57	9.8<H_<12.2	3.0022	Commercial CaO
79.62	9.8<H-<12.2	3.7262	Egg shell-CaO-900
94.52	12.2<H_<15	8.6401	Egg shell-CaO-900-600

Sharma *et al.* (2010) evaluated producing biodiesel by using pongamia pinnata oil transesterification reaction in presence of egg shell as catalyst. They reported that during eggshell calcination at two temperatures catalyst weight increased compared to original weight. The first decreasing observed at 480 °C because of $Ca(OH)_2$ decomposition and the second decreasing observed at 700 °C because of $CaCO_3$ decomposition. Besides, for calcination of eggs shell size of catalyst particles decreased. They reported product rate 95% and conversion rate 97.43% for catalyst optimal condition 2.5 wt% and reaction time 2.5 h, molar ratio of methanol to oil 8:1, reaction temperature 65±5 °C and speed mixer 600 rpm. In this study reported catalyst rate (2.5 wt%) and reaction time (2.5 h) are less than reports from Wei (2009). In another study by Cho and Seo (2010) transesterification reaction of palm oil by using calcium oxide resulted from egg and quail shell as a heterogeneous alkali catalyst has been reviewed. According to results, $CaCO_3$ is the most component of quail and egg shell by rate of 97.3% and 99% respectively, also, small amount of Na_2O, MgO, P_2O_5 and SO_3 reported. They calcined catalysts at different range of temperatures 500-900 °C. At 500 °C quail egg showed higher activity than egg shell. In this study the most proper calcination temperature for egg and quail shell reported as 900 °C and 800 °C respectively. They reported conversion rate 98% for 5 times re-testing by using catalyst in optimal condition molar ratio of methanol to oil 12:1, temperature 65 °C, time 2 h, catalyst rate 1.5 wt% and calcinated temperature 800 °C.

Mollusk shells

Molluscan shell is one of the losses resources that using them avoid polluting environment and help to biodiesel production economically. Study on mollusk shell refers to decade 17th and to the first studies on mollusk anatomy as well (Chateignera *et al.*, 2000; Boro *et al.*, 2012). Mollusk shells are natural ceramic compounds with excellent fracture strength and toughness, which are attributed to their unique microstructures. The shell material is composed of 95-99% crystalline calcite or aragonite (form of calcium carbonate, $CaCo_3$) and protein film which are used as the binder in varying amount from 0.1% to 5% by weight (Boro *et al.*, 2012; Kaplan, 1998).

A molluscan shell can be divided into three primary sections: the other layer is called as periostracum and mainly composed of conchiolins, the middle layer is known as prismatic layer consisting of oriented calcitic crystals and finally the nacreous layer which contains aragonite crystals (Boro *et al.*, 2012).

Rezaei *et al.* (2013) studied on transesterification reaction of soybean by using CaO catalyst which produced from waste mollusk shell of Persian Gulf cost. In this study in order to determine optimal rate of parameters that effective on reaction at 60 °C and 2 h, parameters considered in three low, average and high levels. Optimal rate of molar proportion of methanol to oil 24:1, catalyst amount 12 wt% and calcination temperature of 1050 °C determined for 2 h, in this conditions purity and produced biodiesel reported 100% and 94.1% respectively. Also, catalyst being used in reaction for 5 times and results show that re-calcinating of catalyst caused to decreasing of its activity. The reason that was reported is decreasing of surface and calcium in catalyst with re-calcination. In another study, Hu *et al.* (2011) searched Freshwater mussel shell (FMS) as catalyst applied for producing biodiesel. In this study natural shell, FMS-900 and FMS-900-600 (calcined at 900 °C, 4 h and fully saturated in deionized water and activated at

600 °C for 3 h) evaluated that surface area (BET surface area) for catalysts reported 0.9 m^2/g, 1.5, 32.2 and produced biodiesel (no reaction) 0, 71% and 96% respectively. They reported optimal conditions equal to catalyst rate 5 wt%, proportion of methanol to oil 12:1, temperature 70 °C and reaction time 1.5 h. In addition, in this study catalyst being used in reaction for 7 times and conversion rate of higher than 90% was reported. They stated that freshwater mussel shell can be used as a suitable catalyst with low cost in biodiesel.

Oyster is a food for some countries such as Japan and Korea. Produced shell as a waste material caused to make some problems like environment pollution and disagreeable smell (Boro *et al.*, 2012). Nakatani *et al.* (2009) studied on transessterification of soybean by using calcium oxide catalyst produced from combusted oyster. In this study, oyster shells washed and dried at 110 °C for 2 h after cutting. Oyster shells combusted at different temperatures (100, 500, 700, 800, 900, 1000 °C for 3 h. they reported conversion rate 73.8% for catalyst optimal conditions 25 wt%, reaction time 5 h and temperature 700 °C for 3 h. they also reported that combusted oyster shell can be re-used in higher temperatures.

Shrimp considered as a seafood for many countries. Yang *et al.* (2009) reviewed biodiesel production from rapeseed oil by using heterogeneous from shrimp shell. They prepared a heterogeneous base catalyst by incomplete carbonization of shrimp shell, KF loading and then activation. The best catalyst activity for transesterfication of rapeseed oil to biodiesel was shown the catalyst was prepared by carbonization at 450 °C, KF loading of 25 wt% and activation at 250 °C. It reported that the highest biodiesel conversion of 98.1% could be achieved when the reaction was carried out under reaction conditions of a catalyst amount of 2.5 wt%, a methanol to rapeseed oil molar ratio of 9:1 and a reaction time of 3 h at 65 °C. It was found that the shrimp shell catalyst shows high catalyst activity, ecologically friendly properties and biodiesel production with shrimp shell-derived catalyst leads to minimum pollution and wastes (Sanjay, 2013).

Mud crab is common sea foods used in many countries that its production commercially caused to make shell waste in large scale. Boey *et al.* (2009) evaluated transesterification reaction of palm olein oil by using mud crab as a heterogeneous catalyst. The stated that XRD analysis showed main components of mud crab shell is calcium carbonate, which changed to calcium oxide at 700 °C for 2 h. They reported conversion rate 95.6% for optimal rates mass ratio methanol to oil 0.5:1, catalyst rate 5 wt%, reaction temperature 65 °C, mixer speed 500 rpm and calinated temperature 900 °C for 2 h. Resulted surface area (BET surface area) reported as 13 m^2/g. This amount is much more than surface area of non-calcinated mud crab shell that is equal to 4 m^2/g. In addition, possibility to re-using catalyst for 11 times without any obvious change in catalyst activity with purity of 96.5% is the most considerable result of this reaction.

Biral *et al.* (2012) reviewed biodiesel production from waste frying oil by using heterogeneous catalyst produced from snail shell. In this study, snail shells dried at 110 °C for 24 h after being washed. They calcined at 900 °C for 3.5 h. They reported surface area (BET surface area) 24 m^2/g and reaction kinetics as first time. Also, they reported conversion rate 99.58% and product rate 87.28% for optimal rates molar ratio methanol to oil 6.03:1, catalyst rate 2 wt%, reaction temperature 60 °C for 8 h. they stated that snail shell can be applied as a good source for producing calcium oxide catalyst to produce biodiesel production. Boro *et al.* (2011) in another studies reviewed transesterification reaction of palm oil in the presence of calcium oxide catalyst produced from waste shells of Turbonilla striatula. They reported that CaO at the temperature of 800 °C and calcination at 700-900 °C caused to increasing of surface area and create pore volume higher than at 600 °C. They also reported production rate 93.3% for optimal rates molar ratio methanol to oil 9:1, catalyst rate 3 wt%,

reaction temperature 65 ±5 °C for 6 h.

Boey *et al.* (2011b) reviewed biodiesel production from palm olein oil by using resulted calcium oxide from Cockle shell (Anadara aranosa). They dried Cockle shells at 105°c after several times washing, then calcined them at 900 °C for 2 h. in this conditions, surface area (BET surface area) and pore volume reported as 15 m^2/g and 0.10 Cm^3/g respectively. They reported production rate 97.48% for optimal rates mass ratio methanol to oil 0.54:1, catalyst rate 4.9 wt%, reaction temperature 65 °C for 3 h. they stated that resulted calcium oxide from Cockle shell can be applied as a cheap source for producing commercial biodiesel with ability to at least 3 times re-using by high purity of 96.5%.

Nair *et al.* (2012) reviewed biodiesel production from waste frying oil in presence of calcium oxide that produced from clam shell (*Mereterix mereterix*) as two cheap food and catalyst sources. They calcined calm shells at 900 °C for 2.5 and 3.5 h. Calcination showed higher catalytic activity and low time. By using XRD analysis determined that calm shell includes 97% and little Na, Si, Mn, S, Sr, Al, Fe and has surface area 2.6 m^2/g. they reported production (> 89%) and conversion rate (> 97%) for optimal rates catalyst 3 wt%, molar ratio methanol to oil 6.03:1, temperature 60 °C for 3 h.

Margaretha *et al.* (2012) reviewed biodiesel production from palm oil in presence of calcium oxide resulted from pomacea Sp. Shell. Shells dried at 100 °C after washing, then calcinated at 900 °C for 2 h. XRD showed that catalyst includes plenty amount of CaO (96.83%) and little of other metals. Also, in this study surface area and pore volume reported 17 m^2/g and 0.04 Cm^3/g respectively. Production rate 95.61% reported in optimal conditions molar ration methanol to oil 7:1, catalyst rate 4 wt%, temperature 60 °C for reaction time 4 h. Besides, decreasing of catalyst activity by using re-calcination process is resuscitation.

Xie *et al.* (2008) reviewed calcium oxide production from biont shell as a new source for biodiesel production from rapeseed oil. They used tri-step procedure way including incomplete carbonization (at 500 °C), activation (at 300 °C) and KF impregnation (for 6 h at 25 wt%) and reviewed carbonization effect on concentration of KF solution and activation temperature of catalyst. In this study, they reported biodiesel production rate 97.5% in optimal conditions molar ratio of methanol to oil 9:1, catalyst rate 3 wt%, reaction temperature 70 °C for 3h. They also reported that prepared catalyst from bionet has strong large surface, narrow pore size distribution, relatively broad particle size distribution, long catalyst lifetime and better stability in organic solvent, basicity (Boey *et al.*, 2009).

Other studies done on producing calcium oxide catalyst from mollusk shells. In this regard, a study done by Agrawal *et al.* (2012) on producing biodiesel from frying oil by using calcium oxide prepared from Exoskeleton (*Pila globosa*). In this study they reported that pila globosa shell includes 79.86% Ca and small amount of S, Cr, Sr, Si, Al, W, Sn, Sb, Te, I, Pd. Decomposition of calcium carbonate performed at 860 °C. They reported production 92% and conversion rate 97.8% in optimal conditions molar ration methanol to oil 10:1, catalyst amount 4 wt%, reaction temperature 60±0.5 °C for 5 h.

Animal bones

Studies in the field of producing catalyst from animal bones for producing biodiesel is not to the extent of egg shells and Mollusk shells resources. Animal bones can be used as a catalyst for producing biodiesel (Birla *et al.*, 2012; Boro *et al.*, 2012). Calcium phosphate is the main component of bone and can be transformed to hydroxyapatite which has relatively high catalytic activity, good thermal chemical stability, and can make the production of biodiesel environmentally friendly (Obadiah *et al.*, 2012).

Farooq *et al.* (2015) reviewed producing biodiesel from FFA waste cooking oil by using catalyst from

hen bones. In this study, they boiled bones for 20 min and dried them by sun. Then, washed bones and dried in oven at 110 °C for 6 h. catalyst calcined at three temperatures 800, 900 and 1000 °C for 4 h. At these temperatures, they reported surface area respectively 98.54 m^2/g, 108.74 m^2/g and 120.02 m^2/g for catalysts. They reported conversion rate 89.32% for 5 g catalyst, molar ration methanol to oil 15:1, reaction temperature 65 °C and reaction time 4 h. Also, catalyst used in reaction 4 times and high production rate 80% has been reported in fourth time. In another study, Obadiah *et al.* (2012) reviewed producing biodiesel from palm oil by using catalyst prepared from sheep bones. They calcined catalysts after preparing them at 200-1000 °C. Resulted conversion rate at different temperatures in descending order reported as uncalcined < 200< 400< 1000< 600< 800 °C. They reported conversion rate 96.78% in optimal conditions 20 wt% catalyst, molar ratio methanol to oil 18:1, speed mixing 200 rpm, reaction temperature 65 °C and reaction time 4 h.

Comparison catalyst

Comparing the performance activity of the catalyst will help to a better understanding and careful evaluation. In this field Viriya-empikul *et al.* (2010) reviewed waste shells of mollusk and egg as a catalyst in transesterification reaction of palm olein oil by using three sources waste shells of egg, golden apple snail and meretrix venus and calcining them at 800 °C for 2-4 h. All catalysts showed high activity and production rate higher than 90% of fatty acid methyl ester (FAME) in 2 h by using catalyst rate 10 wt% and temperature 60 °C. Catalyst surface area (BET) reported 0.5, 0.9, 1.1 m^2/g and total pore volume 0.002, 0.004 and 0.005 Cm_3/g respectively. The Ca content in the shell-derived catalyst in descending order was also reported as: egg shell (99.21) > golden apple snail shell (99.05) > meretrix venus shell (98.59) with catalyst activity as follows: egg shell > golden apple snail shell > meretrix venus shell. In another study, Viriya-empikul *et al.* (2012) reviewed calcium oxide prepared from shells of egg, golden snail and meretrix venus (calcined at 700-1000 °C for 0.5-8 h) for producing biodiesel from palm olein oil. Catalyst surface area (BEST) reported 0.9, 0.9, 1.1 m^2/g and total pore volume 0.005, 0.005 and 0.005 Cm^3/g respectively. All catalysts showed high activity and production rate higher than 90% of fatty acid methyl ester (FAME) in 2 h by using catalyst rate 10 wt% and temperature 60 °C. The descending order of the catalytic activity over the shell-derived catalysts (sequenced as egg shell, 94.1% FAME > golden apple snail shell, 93.2% FAME > meretrix venus shell, 92.3% FAME) was attributed to the decrease of specific surface and basic amount of the strong base site. The optimum calcination temperature and time were 800 °C and 2-4 h, respectively. The shorter time and lower temperature caused the incomplete formation of active Ca-based catalysts, while the longer time and higher temperature caused the severe sintering of catalyst particles, resulting in suppressed biodiesel yields. These industrial wastes could stand for promising resources of low-cost catalysts which could bring about the low-cost biodiesel.

Buasri *et al.* (2013) produced biodiesel from palm oil by using calcium oxide prepared from waste shells of mussel, cockle and scallop as a heterogeneous catalyst. They calcined above mentioned shells at 700-1000 °C for 4 h. Catalyst surface area reported 89.91, 59.87, 74.96 m^2/g and pore volume 0.097, 0.087 and 0.130 Cm^3/g respectively. They reported conversion rate near to 95% for all catalysts in optimal conditions molar ratio methanol to oil 9:1, catalyst rate 10 wt% (calcined at 1000 °C for 4 h), reaction temperature 65 °C for 3 h as reaction time. Activity rate and resulted production in descending order of catalyst reported as mussel (97.23)> scallop (96.68)> cockle (94.47). Ability to re-using catalyst for 4 times with production rate of higher than 85% reported. Boey *et al.* (2011c) reviewed producing biodiesel from chicken fat by using calcium oxide prepared from crab and cockle shells (calcined at 900 °C for 2 h). They reported conversion rate 98% in optimal conditions mass ration methanol to oil 0.55:1, catalyst rate 4.9 wt% for 3 h as reaction time. Resulted calcium oxide compound from crab and

cockle shell help to the increasing of product conversion rate in comparison with study done in similar operation conditions on palm oil through Boey (2009) by using crab shell and other study done by Buasri (2013) in higher operation conditions (molar ratio 9:1) on palm oil.

Conclusion

In this review, produced catalysts from renewable animal waste resources evaluated as a heterogeneous catalyst with alkali properties. In this study determined that produced catalysts from renewable animal waste resources have high potential being applied as catalyst to biodiesel commercial producing. General, the main properties of using these catalysts are availability, large resources, renewability, suitable catalytic activity, low expense and re-using ability. Besides, using catalysts produced from heterogeneous renewable animal waste resource cause to omission of hazardous wastes that produced from biodiesel washing and to decrease environmental degradation. Using waste resources for feeding and transesterification reaction catalyst helps to decrease expenses of biodiesel producing and to provide possibility to compete economically with diesel fuel. Generally, it can be said that using catalyst produced from various renewable animal resources in biodiesel industrial production would be suitable in future, but industrial use of them required performing more studies in different types including using them in continuous reactors.

References

Agrawal S, Singh B, Sharma YC. 2012. Exoskeleton of a mollusk (Pila globosa) as a heterogeneous catalyst for synthesis of biodiesel using used frying oil. Industrial and Engineering Chemistry Research **51,** 11875-11880.

Aladetuyi A, Olatunji GA, Ogunniyi DS, Odetoye TE, Oguntoye SO. 2014. Production and characterization of biodiesel using palm kernel oil; fresh and recovered from spent bleaching earth. Biofuel Research Journal **1,** 134-138.

Atabani AE, Mofijur M, Masjuki HH, Badruddin IA, Chong WT, Cheng SF, Gouk SW. 2014. A study of production and characterization of Manketti (*Ricinodendron rautonemii*) methyl ester and its blends as a potential biodiesel feedstock. Biofuel Research Journal **1,** 139-146.

Balat M, Balat H. 2010. Progress in biodiesel processing. Applied Energy **87,** 1815-1835.

Beetul K, Sadally SB, Taleb-Hossenkhan N, Bhagooli R, Puchooa D. 2014. An investigation of biodiesel production from microalgae found in Mauritian waters. Biofuel Research Journal **2,** 58-64.

Birla A, Singh B, Upadhyay SN, Sharma YC. 2012. Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. Bioresource Technology **106,** 95-100.

Boey PL, Maniam GP, Hamid SA. 2009. Biodiesel production via transesterification of palm olein using waste mud crab (Scylla serrata) shell as a heterogeneous catalyst. Bioresource Technology **100,** 6362-6368.

Boey PL, Maniam GP, Hamid SA. 2011a. Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: A review. Chemical Engineering Journal **168,** 15-22.

Boey PL, Maniam GP, Hamid SA, Ali DMH. 2011b. Utilization of waste cockle shell (Anadara granosa) in biodiesel production from palm olein: Optimization using response surface methodology. Fuel **90,** 2353-2358.

Boey PL, Maniam GP, Hamid SA, Ali DMH. 2011c. Crab and Cockle shells as catalysts for the preparation of methyl esters from low free fatty acid chicken fat. Journal of the American Oil Chemists' Society **88,** 283-288.

Borges ME, Díaz L. 2012. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. Renewable and Sustainable Energy Reviews **16,** 2839–2849.

Boro J, Thakur AJ, Deka D. 2011. Solid oxide derived from waste shells of Turbonilla striatula as a renewable catalyst for biodiesel production. Fuel Processing Technology **92,** 2061-2067.

Boro J, Deka D, Thakur AJ. 2012. A review on solid oxide derived from waste shells as catalyst for biodiesel production. Renewable and Sustainable Energy Reviews **16,** 904-910.

Buasri A, Chaiyut N, Loryuenyong V, Worawanitchaphong P, Trongyong S. 2013. Calcium Oxide Derived from Waste Shells of Mussel,Cockle, and Scallop as the Heterogeneous Catalyst for Biodiesel Production. Science World Journal **2013,** 1-7.

Chateignera D, Hedegaardb C, Wenk HR. 2000. Mollusc shell microstructures and crystallographic textures. Journal of Structural Geology **22,** 1723–1735.

Cho YB, Seo G. 2010. High activity of acid-treated quail eggshell catalyst in the transesterification of palm oil with methanol. Bioresource Technology **101**, 8515–8519.

Demirbas A. 2009. Progress and recent trends in biodiesel fuels. Energy Conversion and Management **50,** 14-34.

Dias JM, Alvim-Ferraz MCM, Almedia MF. 2008. Comparison of the performance of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality. Fuel **87,** 3572-3578.

Dizge N, Keskinler B, Tanriseven A. 2009. Biodiesel production from canola oil by using lipase immobilized onto hydrophobic microporous styrene-divinylbenzene copolymer. Biochemical Engineering Journal **44,** 220-225.

Farooq M, Ramli A, Naeem A. 2015. Biodiesel production from low FFA waste cooking oil using heterogeneous catalyst derived from chicken bones. Renewable Energy **76,** 362-368.

Ghanei R, Moradi GR, Taherpour-kalantari R, Arimandzadeh E. 2011. Variation of physical properties during transesterification of sunflower oil tobiodiesel as an approach to predict reaction progress. Fuel Processing Technology **92,** 1593-1598.

Ghanei R. 2014. The changes of physical properties in transesterification of three different vegetable oils to biodiesel; comparison and evaluation to determine reaction conversion. Journal of Biodiversity and Environmental Sciences **5,** 352-361.

Gorji A, Ghanei R. 2014. A review on catalytic biodiesel production. Journal of Biodiversity and Environmental Sciences **5,** 48-59.

Graboaki MS. McComick RL. 1998. Combustion of fat and vegetable oil drived fuels fuels in diesel engines. Progress in Energy and Combustion Science **24,** 125-164.

Guan G, Kusakabe K, Moriyama K. 2009. Transesterification of vegetable oil to biodiesel fuel using acid catalysts in the presence of dimethyl ether. Fuel **88,** 81-86.

Helwani Z, Othman MR, Aziz N, Kim J, Fernando WJN. 2009. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review. Applied Catalysis A: General **363,** 1-10.

Hu S, Wang Y, Han H. 2011. Utilization of waste

freshwater mussel shell as an economic catalyst for biodiesel production. Biomass and Bioenergy **35,** 3627-3635.

Jacobson K, Gopinath R, Meher LC, Dalai AK. 2008. Solid acid catalyzed biodiesel production from waste cooking oil. Applied Catalysis B: Environmental **85,** 86-91.

Jazie AA, Pramanik H, Sinha ASK, Jazie AA. 2013. Egg shell as eco-friendly catalyst for esterification of rapesee oil: Optimization for biodiesel production. Special Issue of International Journal of Sustainable Development and Green Economics **2,** 27-32.

Kansedo J, Lee KT, Bhatia S. 2009. Biodiesel production from palm oil via heterogeneous Transesterification. Biomass and Bioenergy **33,** 271-276.

Kaplan DL. 1998. Mollusc shell structures: novel design strategies for synthetic materials. Biomaterials **3,** 232–236.

Khalili-Darmani R, Syed-Younus S, Mohammadi M, Ghanei R. 2011. Calcium oxide from various sources and evaluation it as a catalyst to produce biodiesel from canola oil. Iran: Tehran; 2011.

Kim M, Yan S, Salley SO, Ng KYS. 2009. The effect of sodium on the catalytic activity of ZnO-Al2O3/ZSM-5 and SnO-Al2O3/ZSM-5 for the transesterification of vegetable oil with methanol. Catalysis Communications **10,** 1913-1919.

Li E, Xu ZP, Rudolph V. 2009. MgCoAl-LDH derived heterogeneous catalysts for the ethanol transesterification of canola oil to biodiesel. Applied Catalysis B: Environmental **88,** 42-49.

Lou WY, Zong MH, Duan ZQ. 2008. Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts. Bioresource Technology **99,** 8752-8758.

Margaretha YY, Prastyo HS, Ayucitra A, Ismadji S. 2012. Calcium oxide from Pomacea sp. shell as a catalyst for biodiesel production. International Journal of Energy and Environmental Engineering **3,** 33-41.

Menetrez MY. 2014. Meeting the U.S. renewable fuel standard: a comparison of biofuel pathways. Biofuel Research Journal **4,** 110-122.

Mighani HM, Almasi M, Bakhoda H, Mohsenfar M. 2009. Comparision physical and chemical properties of methyl ester biodiesel from soybean oil as conventional diesel fuel. Iran: Univercity of Ferdowsi.

Mohadesi M, Hojabri Z, Moradi G. 2014. Biodiesel production using alkali earth metal oxides catalysts synthesized by sol-gel method. Biofuel Research Journal **1,** 30-33.

Mohammadi P, Tabatabaei M, Nikbakht AM, Esmaeili Z. 2014. Improvement of the cold flow characteristics of biodiesel containing dissolved polymer wastes using acetone. Biofuel Research Journal **1,** 26-29.

Montilla A, Castillo MD, Sanz ML, Olano A. 2005. Egg shell as catalyst of lactose isomerisation to lactulose. Food Chemistry **90,** 883-890.

Moradi GR, Mohadesi M, Ghanbari M, Moradi MJ, Hosseini S, Davoodbeygi Y. 2015. Kinetic comparison of two basic heterogenous catalysts obtained from sustainable resources for transesterification of waste cooking oil. Biofuel Research Journal **2,** 236-241.

Nag A. 2008. Biofuels Refining and performance. First ed Mc Graw Hill.

Nair P, Singh B, Upadhyay SN, Sharma YC. 2012. Synthesis of biodiesel from low FFA waste frying oil using calcium oxide derived from Mereterix mereterix as a heterogeneous catalyst. Journal of Cleaner Production **29-30,** 82-90.

Nakatani N, Takamori H, Takeda K, Sakugawa H. 2009. Transesterification of soybean oil using combusted oyster shell waste as a catalyst. Bioresource Technology **100,** 1510-1513.

Niju S, Begum KMMS, Anantharaman N. 2014. Modification of egg shell and its application in biodiesel production. Journal of Saudi Chemical Society **18,** 702-706.

Nurfitri I, Maniama GP, Hindryawati N, Yusoff MM, Ganesan S. 2013. Potential of feedstock and catalysts from waste in biodiesel preparation: A review. Energy Conversion and Management **74,** 395–402.

Obadiah A, Swaroopa GA, Kumar SV, Jeganathan KR, Ramasubbu A. 2012. Biodiesel production from Palm oil using calcined waste animal bone as catalyst. Bioresource Technology **116,** 512-516.

Rezaei R, Mohadesi M, Moradi GR. 2013. Optimization of biodiesel production using waste mussel shell catalyst. Fuel **109,** 534–541.

Sanjay B. 2013. Heterogeneous Catalyst derived from Natural Resources for Biodiesel Production: A Review. Research Journal of Chemical Sciences **3,** 95-101.

Sbihi HM, Nehdi IA, Tan CP, Al-Resayes SI. 2014. Production and characterization of biodiesel from Camelus dromedaries (Hachi) fat. Energy Conversion and Management **78,** 50-57.

Semwal S, Arora AK, Badoni RP, Tuli DK. 2011. Biodiesel production using heterogeneous catalysts. Bioresource Technology **102,** 2151–2161.

Sharma YC, Singh B, Korstad J. 2010. Application of an Efficient Nonconventional Heterogeneous Catalyst for Biodiesel Synthesis from Pongamia pinnata Oil. Energy Fuels **24,** 3223-3231.

Sharma YC, Singh B, Madhu D, Liu Y, Yaakob Z. 2014. Fast Synthesis of High Quality Biodiesel from 'Waste Fish Oil' by Single Step Transesterification. Biofuel Research Journal **3,** 78-80.

Shirazi MJA, Bazgir S, Shirazi MMA. 2014. Edible oil mill effluent; a low-cost source for economizing biodiesel production: Electrospun nanofibrous coalescing filtration approach. Biofuel Research Journal **1,** 39-42.

Simões AS, Ramos L, Freitas L, Santos JC, Zanin GM, De Castro HF. 2015. Performance of an enzymatic packed bed reactor running on babassu oil to yield fatty ethyl esters (FAEE) in a solvent-free system. Biofuel Res J. **6,** 242-247.

Singh Chouhan AP, Sarma AK. 2011. Modern heterogeneous catalysts for biodiesel production:A comprehensive review. Renewable and Sustainable Energy Reviews 15, 4378–4399.

Sohpal VK, Singh A. 2014. Optimization of alkali catalyst for transesterification of jatropha curcus using adaptive neuro-fuzzy modeling. Biofuel Research Journal 1, 70-76.

Strabuck J, Harper GDJ. 2009. Run your diesel vehicle on biofuels: A Do-It-Yourself Manual. First ed. McGraw-Hill.

Suryaputra W, Winata I, Indraswati N, Ismadji S. 2013. Waste capiz (Amusium cristatum) shell as a new heterogeneous catalyst for biodiesel production. Renewable Energy **50,** 795–799.

Tangboriboon N, Khongnakhon T, Kittikul S, Kunanuruksapong R, Sirivat A. 2010a. An innovative CaSiO3 dielectric material from eggshells by sol–gel process. Journal of Sol-Gel Science and Technology **58,** 33-41.

Tangboriboon N, Khongnakhon T, Kunanuruksapong R, Sirivat A. 2010b. An innovative synthesis of calcium zeolite Type A catalysts from eggshells via thesol–gel process. Journal of Inorganic and Organometallic Polymers **21,** 50–60.

Viriya-empikul N, Krasae P, Puttasawat B, Yoosuk B, Chollacoop N, Faungnawakij K. 2010. Waste shells of mollusk and egg as biodiesel production catalysts. Bioresource Technology **101,** 3765-3767.

Viriya-empikul N, Krasae P, Nualpaeng W, Yoosuk B, Faungnawakij K. 2012. Biodiesel production over Ca-based solid catalysts derived from industrial wastes. Fuel **92,** 239-244.

Wei Z, Xu C, Li B. 2009. Application of waste eggshell as low-cost solid catalyst for biodiesel production. Bioresource Technology **100,** 2883-2885.

Xie J, Zheng X, Dong A, Xiao Z, Zhang J. 2008. Biont shell catalyst for biodiesel production. Green Chemistry **11,** 355-364.

Yang L, Zhang A, Zheng X. 2009. Shrimp Shell Catalyst for Biodiesel Production, Energy Fuels **23,** 3859-3865.