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Review Paper

Heterogeneous Catalyst derived from Natural Resources for Biodiesel Production: A Review

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Abstract

Heterogeneous catalysts are receiving more importance for the transesterification of triglycerides present in any oils or fats to produce biodiesel. They are reusable, environmentally benign, could give high quality of products, and more effective than acid catalysts and enzymes for biodiesel production. Recently, heterogeneous catalysts derived from both waste industrial and biological resources have attracted interest for biodiesel synthesis. In this paper, it is attempted to review on recent development and application of low-cost, highly efficient heterogeneous catalysts which are mainly derived from natural resources or waste materials for biodiesel production via transesterification of different oils.

Keywords: Waste materials, renewable resources, heterogeneous catalyst, transesterification, biodiesel.

Introduction

It is impossible for human beings to sustain living standard and economic growth without energy. The worldwide energy consumption is increasing due to rapid population growth and industrial development that causes the price of crude petroleum to rise. The conventional energies such as petroleum-derived fuels, coal and natural gas will be exhausted in the near future and greenhouse gas emission by the usage of fossil fuels is also becoming a greater concern[1-4]. The search of other alternative energies is therefore very important. Recently, alternative energies such as H_2 energy, solar energy, wind energy and biodiesel have been attracted worldwide because of recent energy crisis[5-7]. Biodiesel has been chosen as one of the interesting alternative fuels as it is renewable, biodegradable, non-toxic and environment-friendly fuel. Biodiesel produces lower emission, possesses high flash point, better lubrication, and high cetane number and has very close physical and chemical characteristics to those of conventional diesel fuel allowing its use either on its own (pure biodiesel, B100) or mixed with petroleum based diesel fuel (preferred ratio 5-20%, B5-B20) with very few technical adjustments or no modification[8-13].

Biodiesel is produced from any fat or oil through a process called transesterification. In the production of biodiesel, the triglycerides present in various sources *viz.* edible oil, non-edible oil, animal fats, waste oil and oil from algae are transesterified with methanol in presence of a catalyst (acid, base or biocatalyst) to afford fatty acid methyl esters (FAME) and glycerol as a byproduct[14-28]. The transesterification reaction for biodiesel production can be carried out using both homogeneous (acid or basic) and heterogeneous (acid, basic or enzymatic) catalysts. The base-catalyzed transesterification of oils proceeds faster and give very high yields in short reaction times than that catalyzed by the same amount of an acidic catalyst. Enzyme-catalyzed transesterification is carried out at moderate temperatures with high yields, but this cannot be used for biodiesel production due to high enzyme costs[29]. Although transesterification using an alkaline catalysis process gives high conversion levels of triglycerides to biodiesel in short reaction times, the reaction has several drawbacks. It is energy intensive. Homogeneous base-catalyzed transesterification generates a certain amount of water even if a water-free vegetable oil and methanol is used due to the reaction of hydroxide with methanol. The presence of water leads to the hydrolysis of the esters, and as a result, soap is formed. The formation of soap not only reduces the biodiesel yield but also causes significant difficulty in the separation of ester and glycerol[30-35]. Moreover, in this conventional homogeneous method, the removal of catalysts after reaction is technically difficult and a large amount of waste-water is produced to separate the catalyst and clean the products. Therefore, heterogeneous catalysts are very important for biodiesel synthesis as these catalysts have many advantages over homogeneous catalysts. They are noncorrosive, environmentally benign and present fewer disposal problems. Besides, the use of heterogeneous catalysts does not produce soaps through free fatty acid neutralization or triglyceride saponification. They are also much easier to separate from liquid products, reusable and they can be designed to give higher activity, selectivity and longer catalyst lifetimes[16, 36-41].

The use of a heterogeneous catalyst is promising to reduce the present high production cost of biodiesel making it competitive with petroleum-based diesel fuels. Therefore, research is being directed towards the development of environment friendly and cost-effective heterogeneous catalyst for biodiesel production. Recently, various heterogeneous catalysts derived from renewable materials (natural resources) have been reported in various literatures for conversion of oils to biodiesel and these

are *Musa balbisiana* Colla[42], waste shell of *T. striatula*[43], waste freshwater mussel shell[44], turtle shell[45], waste eggshell[46], waste cockle shell[47], waste shells of mollusk and egg[48], waste fish scale[49], waste mud crab shell[50], chicken eggshells[51], snail shell[52], industrial waste shells of egg, golden apple snail and meretrix venus[53], waste animal bone[54], shrimp shell[55], clamshell (*M. meretrix*)[56], *Pomacea sp*. shell[57], and oyster shell[58]. Most of these waste material derived catalysts are cheap resources of CaO for application as low-cost heterogeneous catalyst for biodiesel synthesis. Previously, these materials were not given importance and were generally considered as waste materials. These catalysts have very high commercial prospects, especially in biodiesel industries, as the catalysts can be prepared at nominal cost from the waste materials reducing the production cost of biodiesel and making it competitive with petroleum diesel. Easy availability, biodegradability and environmental acceptability are other three factors in favour of the catalysts as their large scale use will pose no disposal problem. This discovery and utilization as a catalyst means a value addition to the recycled waste. The catalysts are reusable for several reaction cycles. These catalysts are considered as green-catalyst which is derived from renewable biomasses and the production of biodiesel is also a promising green-process.

In this paper, it is attempted to review on recent development and application of low-cost, highly efficient heterogeneous catalysts which are mainly derived from natural resources or waste materials for biodiesel production via transesterification of different oils.

Heterogeneous Catalyst from Renewable Biomass for Biodiesel Production

Searching and developing economically viable, ecofriendly, and renewable heterogeneous catalysts for biodiesel production is therefore very attractive. Recently, several heterogeneous catalysts derived from renewable resources have been reported (table-1) and showed high potential to be used as a low-cost catalyst for biodiesel production.

Deka *et al.*[42] introduced a novel catalyst derived from the trunk of *Musa balbisiana* Colla (one variety of banana plant) into biodiesel industry and showed that 96 wt.% of the *Thevetia peruviana* seed oil was converted to biodiesel at 32 ^{o}C in 3 h using the catalyst (20 wt.% of oil). The catalyst is heterogeneous and can be easily prepared from the waste of post-harvest banana plants. It is reported that the catalyst is reusable and efficiency of the catalyst is gradually decreased after every recycle. Chemical and spectroscopic investigation showed presence of K^+, Na^+, CO_3^{2-} and Cl^- as major constituents along with eleven other metals *viz*. Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb, which are present only in trace amounts (ppm level). Metals are present as their carbonates, chlorides or oxides. Finely divided carbon particles are also present in the derived catalyst. BET surface area of the catalyst was reported at 1.487 m^2/g.

Boro *et al.*[43] derived solid oxide from waste shell of *Turbonilla striatula* and used as a renewable catalyst for biodiesel production from mustard oil. The catalyst was prepared from shells by calcination at a different temperature range of 600 to 900°C for 4 h and formation of solid oxide (CaO) was confirmed at 800^{o}C. It is reported that transesterification of mustard oil with the shell calcined at 900 °C under the optimum condition of 3 wt.% catalyst, 9:1 methanol to oil ratio at 65±5^{o}C for 6 exhibited the best catalytic activity yielding 93.3% biodiesel. The shells calcined in the temperature range of 700-900 ^{o}C have greater BET surface area and higher pore volume than the shells calcined at 600^{o}C. The catalyst derived from waste shell of *Turbonilla striatula* is reusable and yield decreases with the repeated use in transesterification of mustard oil.

Hu *et al.*[44] derived a low-cost and environmentally friendly heterogeneous catalyst from waste freshwater mussel shell by a calcination-impregnation-activation method and utilized for biodiesel production from Chinese tallow oil. When the reaction was carried out with catalyst (5 wt.% of oil) calcined at 900 ^{o}C at the reaction temperature of 70^{o}C with a methanol/oil molar ratio of 12:1, 96% yield of biodiesel is achieved in 1.5 h. The catalyst was found to be active for 7 times of reuse with the yield of biodiesel more than 90%. The high catalytic activity was also reported and explained by the BET surface area of 23.2 m^2/g for FMS-900-600 (calcined at 900^{o}C for 4 h and completely impregnated in deionized water and then was activated at 600^{o}C for 3 h) versus only 10.5 m^2/g for FMS- 900 (calcined at 900^{o}C for 4 h). This heterogeneous catalyst derived from waste freshwater mussel shell when utilized for biodiesel production can effectively reduce the biodiesel production cost.

Xie *et al.*[45] developed a highly active novel heterogeneous biodiesel catalyst from biont shell by a tri-step procedure: incomplete carbonization-KF impregnation-activation and produced biodiesel from rapeseed oil. The study revealed that the derived catalyst was active for catalyzing transesterification and recyclable. Transesterification of rapeseed oil using 3 wt. % of biont shell catalyst, 9:1 molar ratio of methanol to oil and reaction temperature at 70^{o}C yielded 97.5% biodiesel within 3 h. It is reported that the catalyst derived from biont shell has a large surface area, relatively broad particle size distribution, narrow pore size distribution, strong basicity, long catalyst lifetime and better stability in organic solvent. The catalyst which comes from the natural material, turtle shell, is totally environment-friendly.

Wei *et al.*[46] investigated waste eggshell as low-cost solid catalyst for biodiesel production from soybean oil and showed high activity. The experimental results showed that transesterification of soybean oil with the waste eggshell catalyst calcined at 1000°C under the reaction condition of 3 wt.% catalyst, 9:1 methanol to oil molar ratio at 65^{o}C for 3 h exhibited the best catalytic activity yielding more than 95% biodiesel. Reusability of the catalyst was also investigated for transesterification and reported that the eggshell-derived catalyst

can be repeatedly used for 13 times with no apparent loss of activity. The catalyst gradually loses its activity after being used for more than 13 times. This environmentally friendly, high efficient and low-cost waste eggshell derived catalyst could make the production of biodiesel economically viable making it competitive with petroleum diesel. Boey *et al*.[47] investigated transesterification of palm olein oil to biodiesel with a heterogeneous catalyst (CaO) derived from waste cockle shell (*Anadara granosa*) and reported that more than 97% yield of biodiesel was achieved in 3 h under optimal conditions of 4.9 wt.% catalyst (activated at 900^{o}C for 2 h) and 0.54:1 MeOH/oil mass ratio. The studies revealed that the derived catalyst was highly active for catalyzing transesterification providing another low cost catalyst source for biodiesel industries. The catalyst could be reused for at least three times under the optimized conditions (4.9 wt.% catalyst and 0.54:1 MeOH/oil mass ratio) with purity above 96.5%. Viriya-empikul *et al*.[48] studied and reported that the CaO catalysts derived by doing calcination at 800 ^{o}C for 4 h from three different sources *viz*. eggshell, golden apple snail shell and meretrix venus shell could produce biodiesel from palm olein oil yielding more than 90% in 2 h at 60^{o}C using 10 wt.% catalyst amount. The BET surface area of catalysts prepared from eggshell, golden apple snail shell and meretrix venus shell was respectively reported as 1.1, 0.9 and 0.5 m^2/g. The Ca content in the shell-derived catalysts in descending order was also reported as: eggshell (99.21) > golden apple snail shell (99.05) > meretrix venus shell (98.59) with catalytic activity as follows: eggshell > golden apple snail shell > meretrix venus shell.

Chakraborty *et al*.[49] developed a high-performance, reusable, low-cost heterogeneous catalyst from waste *Labeo rohita* scale (calcined at 600-1000^{o}C for 2 h) for synthesis of biodiesel from soybean oil. Under optimal parametric conditions (methanol/oil molar ratio of 6.27:1, calcination temperature at 997.42^{o}C and catalyst amount 1.01 wt.% of oil), a maximum biodiesel yield of 97.73% was reported. The BET surface area of catalyst obtained was measured at 39 m^2/g and found to possess a basicity of 16.23 mmol of HCl/g of catalyst. The waste fish scale derived heterogeneous catalyst could be reused in transesterification reaction up to six times under optimized conditions indicating a promising low-cost catalyst for biodiesel synthesis.

Boey *et al*.[50] applied waste mud crab (*Scylla serrata*) shell (calcined at 900^{o}C for 2 h) as a highly efficient heterogeneous catalyst to transesterify palm oil into biodiesel. The main component of the shell is calcium carbonate which transformed into calcium oxide when activated above 700^{o}C for 2 h. The optimal conditions reported were 0.5:1 methanol to oil mass ratio, 5 wt.% catalyst amount, reaction temperature at 65 ^{o}C and a stirring rate of 500 rpm. Under the optimized conditions, the reusability of the derived catalyst was examined and found to be active for 11 times of reuse with purity above 96.5% introducing another low-cost catalyst source for producing biodiesel. The BET surface area for calcined catalyst was found to be 13 m^2/g and that for uncalcined catalyst was only 4 m^2/g which indicated the higher activity of the derived catalyst.

Sharma *et al*.[51] prepared a nonconventional heterogeneous catalyst from chicken eggshells and used for biodiesel synthesis from *P. pinnata* oil. The catalyst was prepared from shells by doing calcination at 900 °C for 2 h and solid oxide (CaO) formation was confirmed at 900 ^{o}C. The studies revealed that under the optimized conditions of 8:1 methanol to oil molar ratio, 2.5 wt.% catalyst (eggshell), and 2.5 h reaction time at 65±5 °C, a high biodiesel yield of 95% and conversion of 97.43% was achieved.

Birla *et al*.[52] calcined snail shell at 900 °C for 3.5 h to obtain CaO and examined for transesterification of waste frying oil to produce biodiesel. The calcined snail shell as a heterogeneous base catalyst showed excellent activity with a biodiesel yield of 87.28% and conversion of 99.58%. It is reported that the specific surface area of the derived catalyst was 24 m^2/g and the reaction followed was first order kinetics. It was claimed that snail shell is a novel source for the production of heterogeneous base catalyst that can be successfully utilized for synthesis of biodiesel of high purity.

Viriya-empikul *et al*.[53] derived CaO catalysts (calcined at temperature range of 700-1000 °C for 0.5-8 h) from eggshell, golden apple snail shell and meretrix venus shell. The transesterification of Palm olein oil was conducted using the shell-derived catalysts (10 wt.% of oil) under optimum condition of MeOH to oil ratios (12:1) at 60 °C for 2 h producing more than 90% yield of biodiesel in all the cases. The descending order of the catalytic activity over the shell-derived catalysts with biodiesel yield was reported as follows: eggshell, 94.1 %FAME > golden apple snail shell, 93.2 %FAME > meretrix venus shell, 92.3 %FAME. The optimum calcination temperature was 800 °C for 2-4 h. It was reported that 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 are promising resources for the synthesis of low-cost catalysts for biodiesel production.

Obadiah *et al*.[54] utilized a cost effective catalyst derived from waste animal bones in transesterification of palm oil to biodiesel. The catalyst was calcined at different temperatures of 200-1000 °C and calcining at 200, 400 and 600 °C was not enough to produce highly active catalysts. However, catalyst calcined at 800 °C gave the highest biodiesel yield of 96.78% after a reaction time of 4 h at 65 °C under the optimal conditions of 20 wt.% of catalyst, 1:18 oil to methanol molar ratio and 200 rpm of stirring of reactants. It was reported that the catalyst was reusable and even after the 5th cycle of transesterification, the conversion obtained was 83.7%. It was claimed that the catalyst performed equally well as the laboratory-grade CaO. The catalyst derived from animal bones had excellent catalytic activity, ecologically friendly and certainly could be a cheap catalyst for biodiesel production.

Table-1
Heterogeneous catalysts derived from different natural resources in the transesterification of different oils to biodiesel

Biodiesel feedstock	**Source of catalyst**	**Catalyst preparation/ Calcination temperature (^oC) & time (h)**	**Catalyst amount (wt.%)**	**R.T. (^oC)**	**R_t (h)**	**Y/C (%)**	**Ref.**
Thevetia peruviana seed oil	*Musa balbisiana*	The trunk of *M. balbisiana* was sliced into thin pieces and air dried under sun for several days. Dry material was ignited, allowed to burn and cool down to ambient temperature in its own.	20	32	3	96(Y)	**42.**
Mustard oil	Waste shell of *T. striatula*	600-900, 4	3	65±5	6	93.3(Y)	**43.**
Chinese tallow oil	Waste freshwater mussel shell	200-1000, 4	5	70	1.5	>90(Y)	**44.**
Rapeseed oil	Biont shell	Turtle shell was incompletely carbonized at 200-700 ^oC in a muffle furnace, completely dipped in the solution of KF with different mass ratios in the range of 5-50 wt.% and then activated at 100-700 ^oC in muffle furnace.	3	70	3	97.5(Y)	**45.**
Soybean oil	Waste eggshell	200-1000, 2	3	65	3	>95(Y)	**46.**
Palm olein oil	Waste cockle shell	900, 2	2.2-7.8	R^*	3	>97(Y)	**47.**
Palm olein oil	Waste shells of mollusk and egg	800, 4	10	60	2	>90(Y)	**48.**
Soybean oil	Waste fish scale	600-1000, 2	1-5	70	5	97.73(Y)	**49.**
Palm olein oil	Waste mud crab shell	900, 2	5	65	2.5	*NM*	**50.**
Pongamia pinnata	Chicken eggshells	900, 2	2.5	65±5	2.5	95(Y)/ 97.43(C)	**51.**
Waste frying oil	Snail shell	900, 3.5	1-4	50-65	5-8	87.28(Y)/ 99.58(C)	**52.**
Palm olein oil	Industrial waste shells of egg, golden apple snail and meretrix venus	700-1000, 0.5-8	10	60	2	>90(Y)	**53.**
Palm oil	Waste animal bone	200-1000, *NM*	5-25	65	4	96.78(Y)	**54.**
Rapeseed oil	Shrimp shell	Shrimp shell was incompletely carbonized at 300-500 ^oC in a muffle furnace, completely dipped in the solution of KF with different mass ratios in the range of 15-35 wt.% and then activated at 200-500 ^oC in muffle furnace for 2 h.	2.5	65	3	89.1(C)	**55.**
Waste frying oil	Clamshell (*M. meretrix*)	900, 2.5 or 3.5	3	60	3	>89(Y)/ >97(C)	**56.**
Palm oil	*Pomacea sp*. shell	900, 2	4	60	4	95.61(Y)	**57.**
Soybean oil	Oyster shell	100-1000, 3	5.86-34.14	65-70	1.1-6.8	>70(Y)	**58.**

R.T. = Reaction temperature, R_t=Reaction time, Y = Yield, C = Conversion, NM = not mentioned, R^* = refluxed.

Yang *et al.*[55] prepared a heterogeneous base catalyst by incomplete carbonization of shrimp shell, KF loading, and then activation. The best catalytic activity for transesterification 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 is reported that the highest biodiesel conversion of 89.1% could be achieved when the reaction was carried out under the reaction conditions of a catalyst amount of 2.5 wt %, a methanol/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 catalytic activity, ecologically friendly properties and biodiesel production with shrimp shell-derived catalyst leads to minimum pollution and wastes.

Nair *et al.*[56] calcined clamshell (*M. mereterix*) at 1173 K for 2.5 and 3.5 h and utilized as a heterogeneous catalyst to produce biodiesel from waste frying oil. The catalyst calcined for 3.5 h showed higher activity and reduced transesterification reaction time. It was reported that the major constituent present in the catalyst was calcium (97%) along with a few minor elements (Si, Na, Fe, Al, Sr, S, Mn) and the surface area of the catalyst was found to be 2.6 m^2/g. Under the optimum reaction conditions of 3 g of catalyst and 25 ml of methanol per 100 ml of oil (6.03:1, methanol to oil molar ratio) at a reaction temperature of 333 K, a high biodiesel yield (>89%) and conversion (>97%) were achieved in 3 h. It is claimed that this process of biodiesel synthesis is a green process as the raw materials used for this reaction are also waste materials (waste frying oil as biodiesel feedstock and calcined clamshell as catalyst).

Margaretha *et al.*[57] conducted calcination of *Pomacea sp.* shell at 900°C for 2 h to obtain CaO catalyst and investigated transesterification reaction of palm oil to produce biodiesel. It was reported that the maximum yield of 95.61% biodiesel was achieved on the following reaction conditions: reaction temperature of 60°C, a reaction period of 4 h, a ratio of methanol-oil at 7:1, and amount of catalyst at 4 wt.%. XRF determination showed that the catalyst mainly consists of CaO (96.83%) with small amount of other metal as impurities. Reported BET surface area was 17 m^2/g and the activity of spent catalyst could be restored by re-calcination process.

Nakatani *et al.*[58] examined transesterification of soybean oil catalyzed by combusted oyster shell and found to be active, reusable and comparable to that of CaO. The waste oyster shell was combusted at different temperatures of 100, 500, 700, 800, 900 and 1000 °C for 3 h and reported that the catalytic activity of combusted oyster shell at and above 700 °C was identical to those of CaO. Under the optimum reaction conditions of catalyst amount of 25 wt.%, reaction temperature at 65-70 °C, reaction time of 5 h, the yield of biodiesel achieved was more than 70%.

Conclusion

In this review, the heterogeneous catalysts derived from renewable resources have been presented and showed increasing interest for biodiesel synthesis. It is learned from the present review that availability, reusability, catalytic activity and lower cost are extremely important to be a successful commercial catalyst as these have a direct effect on production cost of biodiesel. This heterogeneous catalyst has very high commercial prospects, especially in biodiesel industries, as the catalyst can be prepared at nominal cost from the waste materials. Application of this waste materials is an interesting area of research and considered as excellent raw materials for the preparation of catalyst for biodiesel production due to their wide source and cheap. These heterogeneous catalysts are biodegradable, environmentally benign, their large scale use will pose no disposal problem and the discovery means a value addition to the waste generated. These could eliminate the wastes and produce biodiesel with cost-effectiveness. In addition to biodiesel production, these ecofriendly waste catalysts may also find application in some other organic reactions.

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