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Review Article

A review on biodiesel production using eggshell as catalyst

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ABSTRACT

Transesterification of fatty acid methyl ester (FAME) is the most known production method of biodiesel which has a growing popularity in the renewable clean energy sector. Energy consumption increases all around the world. To meet increasing this consumption lots of new techniques are being studied. It is important to obtain low cost and high quality energy. For biodiesel production processes it can be provided by improving reaction conditions. Conversion efficiency of transesterification process is an important parameter so various catalysts are being developed to increase it. Waste materials are good alternatives for catalyst production. There are lots of studies are being carried about using waste materials as catalyst. Cost of energy decreases and waste assessment is provided by this way. Among the heterogeneous catalysts, calcium (Ca) based catalysts are highly preferred in the transesterification reaction because of their high catalytic activity and easy accessibility. It can be obtained from especially egg shell and egg is one of the most over-consumed foodstuff across the world. Waste egg shell that is rich in terms of Ca was subjected to calcination process to obtain calcium oxide (CaO). CaO catalyst which is synthesized with high activity increased the quality of reaction. In this study efforts have been taken to review the studies that are about the biodiesel production from vegetable oil using waste egg shells as a bio-based catalyst. Optimum experimental conditions were summarized from reviewed studies.

Keywords: Biodiesel, Eggshell, Calcium oxide, CaO, Bio-based catalyst

1. Introduction

Nowadays, researchers have focused on biofuels such as biodiesel and bioethanol as an alternative to conventional fossil fuel [1]. Among lots of renewable energy sources (such as hydrogen, solar, wind and others), biodiesel is one of the most well-known alternative fuels due to its clean, renewable and environment friendly nature [2]. Besides, biodiesel presents many advantages such as a high cetane number, high flash point, lubricity properties, biodegradability and environmentally friendliness [3-4]. Although there are many methods in biodiesel production, the easiest and most cost-effective method is transesterification [5-7]. Transesterification reaction is the reaction of vegetable or animal fats with a short chain alcohol in the presence of catalyst to form FAME and glycerol [8-9]. The purpose of this reaction is produce less viscose and more volatile fuel [10-11]. The transesterification process has some difficulties due to presence of free fatty acids (FFA) and water content. Thus requires high quality raw materials to avoid side reactions and saponification [11-12]. Transesterification can be catalyzed with alkali, acid or enzyme catalysts. Each has various advantages and disadvantages so, it will be correct to choose according to raw materials and working conditions

[13]. These are basically divided into two classes as homogeneous and heterogeneous catalysts [9]. The conventional catalysts are alkali metal hydroxides and alkoxides namely homogeneous strong bases and homogeneous acids such as H_2SO_4 [11, 14]. Alkali-catalyzed transesterification is much faster than acid-catalyzed [15]. Homogeneous base catalysts generally cause to corrosion in the equipment and also leading to the formation of undesired by-products that requires separation steps. This extra separation step increases the cost. Homogeneous acid catalysts are difficult to recycle and operate at high temperatures. They also cause corrosion and serious environmental problems. Novel technologies that cope with problems such as corrosion and toxicity related to homogeneous catalysts are based on the use of heterogeneous catalysts in the transesterification process [4, 14, 16]. In this study efforts have been taken to review the studies that are about the biodiesel production from vegetable oil using CaO, a bio-based catalyst.

2. Heterogeneous Catalysts

Solid catalysts can be examined in two titles, acidic and basic. Basic catalysts are metal oxide, mixed oxide and hydrotalcite [13, 17]. On the other hand, transition metal oxide, ion exchange resin, carbon based catalyst and zeolites are among the acidic catalysts [18]. Although the preparation of high-yield solid catalysts is complex and costly, the benefits of being environmentally friendly, reusable in continuous processes, either directly or as a result of additional processing, and long catalyst life can be counted as advantages [7, 9, 14]. These catalysts neither dissolve nor deplete in the reaction mixture, which makes it easier to leave the product after transesterification [19]. The recovered catalyst can be reused in the reaction so that the cost associated with catalyst consumption is reduced [1]. As a result, purification of the products is simplified because no washing with water is necessary to separate the catalyst, and a very high ester yield is obtained near the theoretical value [13]. Thus, glycerol is produced directly in high purity (at least 98%) and does not contain any salt contaminants [4, 20]. Catalyst manufacturing cost can be a critical factor in industrial applications. In order to make the biodiesel production process economically and ecologically suitable, an efficient and cheap catalyst production is required. In this way, it is demanded that the price of the final product can be reduced to a level that can compete with petroleum diesel [21-23]. The presence of three unmixed phases in the use of solid catalyst (solid catalyst-alcohol-oil) limits the mass transfer efficiency, thereby reducing the reaction rate [3]. In addition, most of the solid catalysts have problems such as a small number of active sites, micropores, high cost, non-renewable sources and not being environmentally friendly [1, 24]. Therefore, it would be beneficial to produce a low cost solid base catalyst having an active surface area and a large pore diameter in order to eliminate all these disadvantages [1, 25].

2.1. Bio-based CaO catalyst

Bio-based catalyst is defined as a type of catalyst derived from natural sources such as biomass. Recent studies have shown that biological source such as calcium and carbon becomes a potential heterogeneous catalyst for biodiesel production process. This is a promising method because highly efficient bio-based catalysts come to exist at the end of this application. The biomass originated solid catalysts are non-toxic, non-corrosive so presents an environmentally friendly solution and eliminate the production of wastewater [1, 26]. The catalyst is biodegradable so it is not cause any disposal problem [27].

Calcium compounds which are among the base solid catalysts have been used in various forms (oxide, hydroxide, carbonate, and diglyceroxides) in transesterification reactions. CaO is an environmentally friendly material that classified in heterogeneous base catalyst. Commonly, it can be derived from $CaCO_3$, $Ca(NO_3)_2$ or $Ca(OH)_2$ raw materials. Generally, limestone is used for obtain CaO but the length and cost of the synthesis route become a problem. In addition, this route is not prefer because of its non-renewable nature [28]. Because of these, a catalyst derived from organic waste materials has gained much attention due to its nontoxic, abundant, low cost and renewable nature [1]. These materials can be obtained from several natural sources such as eggshell, animal bone and mollusc shell etc. In order to provide cost effective production, waste materials good alternatives for bio-based catalyst production [8-11, 29].

Recent studies have focused on the production of biodiesel using waste shells as catalysts. Wei et al. [14] was studied for transesterification of vegetable oil with egg shell as catalyst. This study was a precursor of the easy way of green catalyst synthesis. In the light of this work many researchers have also proposed the utility of this bio-based catalyst not only for biodiesel production but also in other fields of catalysis. According to many researchers these materials very important because of its reusability [14].

Egg shells consist of mainly calcium carbonate (94 %) and other secondary materials like magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) [30]. Egg is one of the most over-consumed foodstuff across the world and has an egg shell that is rich in terms of Ca. Calcium oxide (CaO) catalyst which is synthesized by calcination of egg shells is used to evaluate waste shells and increase the quality of reaction. The structure of eggshell is suitable for preparation of active heterogeneous catalyst due to its porous structure and its high content of $CaCO_3$ [14]. Upon

calcination of eggshell, $CaCO_3$ converts into CaO and also its activity increases based on change of the surface structure [1].

Catalyst Preparation: Catalyst preparation was carried out by calcination method. Eggshells are converted to powder form for successful calcination process. Then, heat treatment is applied to the powder. The condition of the calcination step is very important. Appropriate temperature and reaction time supplies active catalyst production. For quality calcination sample should be uniform. Fig. 1 illustrated the preparation process of waste-eggshell derived catalyst.

Figure 1. Preparation of CaO catalyst derived from eggshell waste [31]

Upon calcination process, characterization of catalyst is very important. Eggshells consist of $CaCO_3$ as a major component and after calcination this material should convert to CaO. For characterization of the catalyst XRD analysis can be practised. Fig. 2 shows XRD patterns of a natural eggshell and catalysts obtained from calcination at different temperatures. $CaCO_3$ is major component up to 800ºC as shown. Some CaO peaks come up at 700ºC but good conversion is shown beyond 800ºC.

As shown in Fig. 2 Calcination step resulted in a change in the XRD pattern for different temperatures. Because CO_2 move away from the starting material due to thermal treatment. The diffraction patterns of the samples heated above 800°C were related to CaO, while samples heated at temperatures below 800°C, were related to $CaCO_3$. The aim of calcination process is conversion of $CaCO_3$ to CaO so calcination temperature should be above 800ºC [31]. Wei et al. [14] were calcined eggshell between 200ºC -1000ºC and tested this catalyst for transesterification of soybean oil to produce biodiesel. According to these results the catalyst which was calcined above 800ºC was the most active catalyst. The conversion efficiency was obtained 97-99 % with this catalyst. Besides, as the temperature decreases the yield of transesterification reaction decreases. Below 600ºC calcination temperature the yield was obtained 30% [14].

Jazie et al. [32] was investigated calcined eggshell as a solid catalyst for use in production of biodiesel based on rapeseed oil. BET analysis results of calcined eggshell were shown that BET surface area of catalyst was high (59.0717 m^2/g) at 900ºC calcination temperature. This value was 3.4056 m^2/g and 4.7966 m^2/g at 800ºC and 1000ºC, respectively. A yield of 96% was obtained in the presence of eggshell catalyst calcined at 900ºC, while it was 90% at 1000ºC. The BET studies confirmed that the particle size decreased as the calcination temperature increased [32].

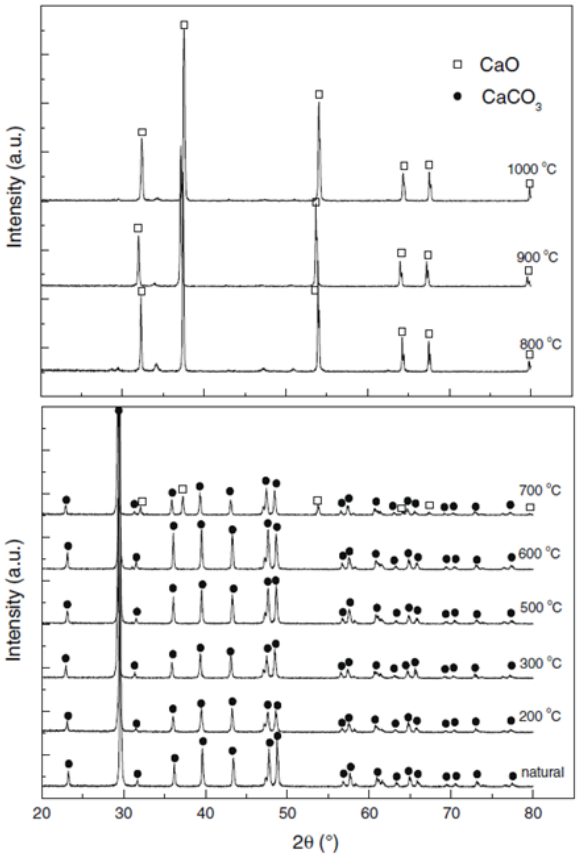

Figure 2. XRD patterns of natural eggshell and the materials obtained by calcining natural eggshell in the range of 200ºC–1000ºC [14].

Viriya-empikul et al. [29] were examined the effect of calcination time (0.5, 2, 4, and 8 hours) on reaction yield. Bio-based CaO catalyst was used and it was found that 30 minutes calcination time was not enough to produce active catalyst. The samples were calcined for 2–4 hours exhibited adoptable activity. Furthermore, more increase in calcination time effected the catalytic activity of the catalyst inversely [29].

Biodiesel Production: Farooq et al. [37] studied preparation of an efficient catalyst from waste chicken eggshells. This study aims exploring environmentally friendly and cost-effective biodiesel production conditions. Catalysts were prepared from waste eggshell powder at three different temperatures (800°C, 900°C and 1000°C) in a muffle furnace. Catalyst which is synthesized at 900 °C was called as C900. According to the BET surface area and pore volume of C900 were found to be relatively higher as compared to the catalysts synthesized at 800°C or 1000°C. It means this catalyst provides better catalytic activity in date seed oil transesterification reaction for efficient biodiesel production.

Hence C900 catalyst was chosen for optimization of biodiesel parameters. They used date seed oil, 5 wt. % catalyst, 12:1 methanol: oil ratio and conversion efficiency was obtained 93.5 % at the end of 1.5 hour [37].

Wei et al. [14] studied effect of calcination temperature on structure and activity of eggshell catalysts. They were calcined eggshells in the muffle furnace at different temperatures (200ºC –1000ºC) for 2 hours. Transesterification reaction was performed with soybean oil. According to experimental results 9:1 molar ratio of methanol to oil, with 3 wt% eggshell-derived catalysts (calcined at 1000ºC, CaO), 65ºC reaction temperatures gave the best results, and the biodiesel yield exceeded 95% at 3 h [14].

Correia et al. [28] examined the activity of waste eggshell and crab shell in the transesterification of sunflower oil. Calcination reaction was performed at 900°C for 2 hours for the conversion of $CaCO_3$ into CaO. Eggshell resulted in 97.75% of FAME yield under reaction conditions of 3 wt% catalyst load, methanol-to-oil ratio of 9:1 and 3 h reaction time. On the other hand, crab shell showed FAME yield of 83.1%. Eggshell catalyst performed better catalytic activity than that of crab shell. This is because the eggshell has higher surface content of Ca during calcination process [28].

Viriya-empirikul et al. [29] studied the performance of three types of waste shells. Transesterification of palm olein oil was performed with waste shells of egg, golden apple snail, and meretrix venus catalysts. They were calcined at 800°C for 0.5–8 h. After 1 h reaction, the yield of biodiesel using waste eggshells, golden apple snail, and meretrix venus were 93, 86 and 74%, respectively. Eggshell showed excellent ability as a catalyst compared to others. Upon 2 h reaction, all catalysts provide greater than 90% yield [29].

Jazie et al. [32] were investigated calcined eggshell in rapeseed oil transesterification. A quadratic polynomial equation was obtained for biodiesel yield by multiple regression analysis. The optimum conditions; 9:1 molar ratio of methanol to oil, 3 wt% calcined eggshell catalyst (calcined at 900ºC, 2 h), 60ºC reaction temperatures at reaction time of 3 h were specified. To confirm accuracy of this model, egg shell catalyzed transesterification was carried out. Experimental results were shown that the yield of reaction was 96% and also predicted biodiesel yield was calculated as 95.89% from the model. Thus, results of experiments confirmed the validity of the predicted model [32]. Table 1 summarizes conversion efficiencies, catalyst synthesis and reaction conditions that were obtained from reviewed studies are investigated.

Table 1. Bio-based CaO catalyst for biodiesel production

		Catalyst Preparation Condition		Transesterification Reaction				FAME	References
Catalyst	**Feedstock**	**CT (ºC)**	**Ct (h)**	**T (ºC)**	**t (h)**	**C (wt.%)**	**M:O**	**Yield (%)**	
Waste chicken eggshell	Palm olein oil	800	2-4	60	2	10	18:1	94.1	[29]
	Soybean oil	900	3	25	9	5.8	6:1	96	[33]
	Cooking oil	900	2	60	5	4	24:1	100	[34]
Chicken eggshell	Sunflower oil	900	2	60	3	3	9:1	97.8	[28]
	Palm oil	900	4	60	4	20	9:1	94.4	[31]
	Soybean oil	1000	2	65	3	3	9:1	95	[14]
	Waste frying oil	900	2,5	65	1	5	12:1	94.5	[35]
	Rapeseed oil	900	2	60	3	3	9:1	96	[32]
Duck eggshell	Palm oil	900	4	60	4	20	9:1	92.9	[31]
Commercial CaO	Jatropha Curcas	900	1.5	70	2.5	1.5	9:1	93	[36]

CT: Calcination temperature, Ct: Calcination time, C: Catalyst amount, M:O: Methanol to oil ratio

According to Table 1, 900ºC is a good calcination temperature. Based on the previous works that have been carried out, it was determined that 2 h calcination process resulted with a high yield of transesterification reaction. It is reasonable that for cost effective production process, 9:1 molar ratio and 3 wt.% catalyst amount can be preferred for high FAME yield. Approximately 3 h of transesterification reaction provides high efficiency.

Reusability of Catalyst: Reusability of catalyst varies for different feedstock and operation conditions.

Jazie et al. [32] revealed that the catalyst can be repeated use for 14 times with no apparent loss of activity. After the 14th cycle of transesterification with same catalyst, the yield was 88%. But after being used for more than 14 times, catalyst lost activity gradually. They were used catalyst more than 18 times and the catalyst was completely deactivated. They were examined this deactivated catalyst and XRD patterns showed $Ca(OH)_2$ as major component. This is because of the reaction between H_2O (from methanol and vegetable oil) and CaO [32].

Wei et al. [14] also revealed that the catalyst can be used more than 1 cycle. They also investigated the reusability of the catalyst. The results indicated that the eggshell-derived catalyst can be used repeatedly for 13 times with no apparent loss of activity. The catalyst lost activity gradually after being used for more than 13 times. It was completely deactivated after being used more than 17 times. They also claim that deactivation of catalyst due to $Ca(OH)_2$ formation [14].

3. Future Perspective

The utilization of biomass-derived heterogeneous CaO catalyst for biodiesel production seems to be a promising choice. Because it extinguishes problems faced by homogeneous operations. The use of waste materials as the source of catalyst may reduce the cost of biodiesel production process and also provide new applications for the waste materials. However, further investigation and development of bio-based catalyst are necessary to be improved the catalytic performance for biodiesel production as well as other chemical processes.

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