Modification of Eggshell and Seashell Wastes as catalyst in Biodiesel Production

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Abstract

In recent years, the used of catalyst had become a norm to speed up the production of biodiesel from vegetable oils. In this work, egg-seashell wastes which are rich in calcium oxide (CaO) are used as catalyst to accelerate the production of biodiesel from palm oil. The catalysts were prepared via calcination method at 400°C, 500°C, 700°C, 900°C and 1000°C for 1.5 h, 2.5 h and 3.5 h for each consecutive temperatures. The experimental parameters were reaction time, reaction temperature, methanol/oil molar ratio and catalyst loading on the transesterification for the production of biodiesel has been also consider to get higher yield. All the parameters were proceeded by 5 wt% of catalyst, methanol to oil ratio was 2:1 and a reaction temperature of 65° C with reaction time of 1 h. The catalyst performance is measured according to their conversion percentage. Under the possible optimum reaction conditions, the highest conversion achieved was 85.7%.

Keywords: biodiesel, calcium oxide, calcination-hydration-dehydration, egg-seashells, transesterification, palm oil.

1. Introduction

The demand of fossil fuel production is being dramatically increased for transportation usage. It has prompt the need of a crucial research for finding an alternative fuel for diesel engine as a replacement for the fossil fuel that we use today. Fossil fuel can contribute pollution to the environment such as the global warming. It is also one of the major sources of greenhouse gas emission as well (Endalew et al., 2011). Fossil fuel is a natural source that is not capable of being replenished, and therefore it's total quantity is inching ever so closely towards depletion. In order to overcome these problems, biodiesel is proposed in our industry for diesel engine.

Factors to be considered for the alternative fuel are renewable, economic feasible and environmental friendly. Biodiesel is the best alternative fuel because it can fulfill the considered factors, convenient and no adverse effect to public health. Biodiesel is non-toxic, biodegradable and can reduce the gas emission to surrounding (Vyas et al., 2010). In addition, production of biodiesel requires a big budget due to high price of catalyst used. Besides, the used of edible plant and vegetable oil as raw materials is also high cost. Non-edible plant and waste oils which are animal fats, fish oil, vegetable oil (waste) as raw materials can reduce the cost of biodiesel production. The main objective of the biodiesel usage is to improve better quality of exhaust gas emission and reduce pollutions (Glisic & M Orlović, 2013). Biodiesel have a high flash point which is easy to handle and good lubricity (Kouzu & Hidaka, 2012), (Glisic & M Orlović, 2013). Malaysia is the world's second largest palm oil plantation (Tshizanga et al., 2017) so, it is beneficial to use the oil to make biodiesel as fuel for diesel engine in order to reduce pollutions.

To produce the biodiesel, the types of catalyst such as homogenous, heterogeneous, acidic or alkaline have been studied to determine its pros and cons. Catalyst can broadly be defined as a substance that increases the rate of reaction without itself undergoing any permanent chemical changes. Presence of catalyst in biodiesel production can give rise to the reaction rate and yield. Transesterification process is the method used to breaks down the chemical structure of triglycerides in oil to form biodiesel (Colombo et al., 2017) by using acidic or alkaline catalyst (Niju et al., 2014). This process involved of waste vegetables oil or animals fat and a short chain of alcohol such as methanol or ethanol to obtain fatty acid alkyl esters (FAMEs) which also known as biodiesel and glycerol as by-product (Ke·ic et al., 2016).

Previous studies of catalyst showed that alkaline catalyst is considerably faster than acidic catalyst and it is the most common applied in biodiesel production. Homogeneous catalyst is being used in the transesterification process which resulted high yield and conversion of biodiesel at a mild temperature, atmospheric pressure and shorter reaction time but these catalysts have several problems such as separation of the catalyst after reaction, generation of excess wastewater, emulsification and more energy consumption (Niju et al., 2014).

As a solution to these issues, the idea of heterogeneous catalysts had been developed. There are several advantages of heterogeneous catalysts which are simple catalyst recovery, reusability of the catalyst, simple product purification and less energy and water consumption. Heterogeneous solid catalysts include alkaline earth metal oxides such as calcium oxide (CaO), magnesium oxide (MgO) and hydrotalcites (Tshizanga et al., 2017) and other single metal oxides such as zinc oxide (ZnO), tin dioxide (SnO_2) and cerium IV oxide (CeO_2).

Among the heterogeneous solid catalysts, calcium oxide (CaO) is one of the most promising catalyst with a good performance in biodiesel production. This is due to the elimination of neutralization step, high catalyst activity, being active in mild reaction conditions, long catalyst life time, low solubility in methanol, lack of toxicity, ability to withstand higher temperatures, can be easily recycled, low cost, easily obtained and its availability which abundance in our nature (El-Gendy et al., 2014).

However, most of heterogeneous catalysts has their own limitations which require a longer reaction time, high reaction temperature and low catalytic stability which gives low yield of biodiesel due to slow reaction rate (Wei ėt al., 2009). (Niju et al., 2014) studied the transesterification of waste frying oil using CaO as a heterogeneous catalyst and achieved a high biodiesel conversion of 94.52%. The catalyst underwent the calcination-hydration-dehydration treatment which under these conditions, CaO catalyst exhibited the greatest catalytic activity and produce high yield of biodiesel. The studied was carried out by depending on the methanol/oil ratio, catalyst loading and reaction temperature (Tshizanga et al., 2017).

In addition, CaO can be produced from waste of seashells and eggshells. The solid waste underwent the calcination-hydration-dehydration treatment to transform into CaO as catalyst. A study had proven that high biodiesel yield of 100% is obtained using 4wt% of the modified eggshell as catalyst for a reaction time of 5 h in the transesterification of used cooking oil (Navajas et al., 2013). Besides, a study that are used oyster shells for the transesterification of soybean oil is obtained a biodiesel yield of 73.8% using 25wt% catalyst for a reaction time of 5 h (Nakatani et al., 2009). From this research, several studies are also applying the combination of eggshell and seashell as their catalyst for the biodiesel production. The utilization of eggshell and snail shell for the transesterification of palm oil produced biodiesel yield above 90% using 10wt% catalyst for a reaction time of 2 h (Viriya-empikul et al., 2012).

The previous study focused towards the development of highly active CaO catalyst obtained from eggshells and seashells such as oyster on calcination-hydration-dehydration treatment. The objectives of this experiment is to produce highly active CaO catalyst from eggshells and the mixture of seashells (snail and oyster) in order to obtain high yield of fatty acid methyl esters (FAMEs).

2. Methodology

2.1 Materials

The main materials to be used are eggshell and seashell wastes. Eggshell wastes were collected at UiTM Pasir Gudang cafe and seashell wastes were collected at Senibong Cove restaurant, Johor Baharu. Besides, palm oil was purchased from local market nearby Pasir Gudang.

2.2 Catalyst preparation

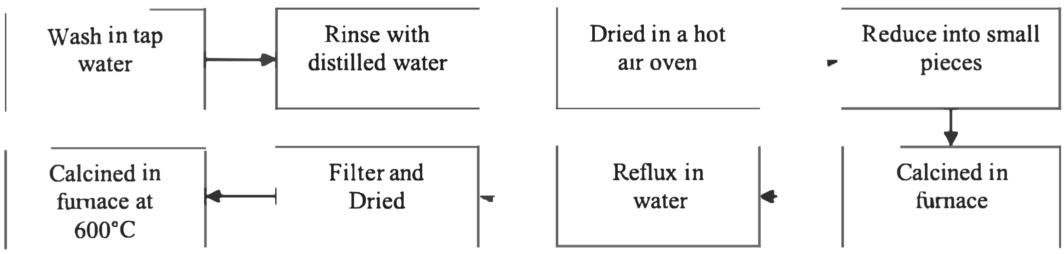

Figure 1: Steps to prepare egg-seashells catalyst

The eggshells and seashells were washed thoroughly in tap water to remove impurities and any unwanted waste on its surfaces, and rinsed with distilled water. The washed egg-seashells were then dried under sunlight for a day to remove unpleasant odor. Then, the egg-seashells were put in an oven at 105°C for 24 hours. The dried egg-seashells were grinded into small pieces until it becomes powder to increase the surface area. Then, the egg-seashells powder is put in a crucible for calcination process in a muffle furnace (Nuve-MF 106 Philipines) under static air conditions at 400°C, 500°C, 700°C, 900°C and 1000°C for 1.5 hours, 2.5 hours and 3.5 hours. Then, the CaO derived from the egg-seashells were refluxed in water at 60°C for 6 hours and the solid particle was filtered and dried in an oven at 120°C for overnight. The solid particle was dehydrated by undergoes calcination process at 600°C for 3 h to change the hydroxide form to oxide form.

2.3 Transesterification process

Transesterification process is used to produce biodiesel. The biodiesel is produce by using two different catalysts which are sodium hydroxide (NaOH) and egg-seashell respectively but the same alcohol is used namely methanol. Basically, the process to produce biodiesel depends on the type of catalyst applied.

For sample that use sodium hydroxide (NaOH) as catalyst required 100 ml of palm oil, 0.6 grams of NaOH and 25 ml of methanol. The procedure was carried out by heating the oil until it reached temperature 55°C before pour into methoxide. At 37°C, 0.6 grams of NaOH was added into the 25 ml of methanol. Then, mix them together until NaOH cannot be seen in the methanol. Methoxide was produced after NaOH and methanol is completely mixed. Then, the heated palm oil is pour into a beaker with methoxide. The beaker must be sealed to ensure that the mixture does not spilt out of the beaker during shaking for 15 seconds. Transesterification process was occurred while leaving the sample for a day.

Next, for sample that used egg-seashell as catalyst need to prepare 100 ml of palm oil, 25 ml of methanol and 4.1335 grams of egg-seashell catalyst. The weight of catalyst is determined by 1:1 ratio of eggshell to seashell. The procedure was carried out by heating the palm oil on heating mantle until reached temperature 105°C. Then, egg-seashell catalyst is added into the heated oil and stir vigorously in a few minute until the catalyst mixed well. After that, let the mixture to cool down until 65°C and then methanol is added into the oil. The oil temperature will drop and need to heat up again to 65°C and keep stirring until reached the desired temperature. The temperature must constant for 1 hour. Last but not least, switch off the heating mantle and leave the sample for one or two days for transesterification process. Method applied to egg-seashell catalyst is repeated with different catalyst preparations properties. The amount of separate biodiesel and glycerol was recorded to compare the yield of biodiesel produced at different catalyst.

2.4 Biodiesel production

After leaving the mixture of biodiesel and glycerol for a day, the product will form two layers which are biodiesel and glycerol. The upper layer is biodiesel or known as fatty acid methyl ester (FAME) and the bottom layer is glycerol. Basically, the biodiesel and glycerol need to be separated to determine the biodiesel produced. The biodiesel and glycerol were transferred into a measuring cylinder to measure the volume of biodiesel and glycerol. After that, the biodiesel and glycerol were transferred into a small bottle as our sample review. The best sample is chosen and will be compared with other samples.

3. Results and discussion

3.1 Hydration-calcination-dehydration process

Egg-seashells catalysts (CaO) were employed for biodiesel production via transesterification of palm oil. The reaction was performed with a 5 wt% of catalysts, methanol/oil ratio of 12:1, a reaction temperature 65°C and reaction time of 1 h. In this study, the parameters involved are temperature and time. The egg-seashells catalysts were calcined at different temperature and time to compare the activity of CaO on transesterification process of palm oil and methanol. The temperatures are 400°C, 500°C, 700°C, 900°C and 1000°C and the times are 1.5 h, 2.5 h and 3.5 h. The relationship between the parameters studied and their combinations are according to their influence on the conversion to methyl esters (Colombo et al., 2017).

Formation of CaO catalyst from egg-seashells was confirmed by calcination step as at temperature 400°C, 500°C, 700°C, 900°C and 1000°C. Basically, calcination process is to convert the calcium carbonate ($CaCO_3$) in the shells into CaO particles. Then, the CaO derived from the egg-seashells were refluxed in water at 60°C for 6 h and the solid particle was filtered and dried in a hot air oven at 120°C for overnight (Yoosuk et al., 2010). The solid particle was dehydrated by undergoes calcination process at 600°C for 3 h to transform the hydroxide form to oxide form. Thus the mixture of egg-seashells subjected to the calcination-hydration-dehydration treatment generate a highly active CaO (Niju et al., 2014).

Biodiesel and glycerol are products that result from transesterification process. Theoretically, the products were determined by the formation of two layers after the mixture were allowed to settle overnight. The top layer of the product is fatty acid methyl ester (FAMEs) or known as biodiesel and the bottom layer is glycerol. The two layers are clearly seen due to the density of biodiesel and glycerol. The density of biodiesel is 830 kg/m3 and the glycerol is 1126 kg/m3 respectively. Based on the density, biodiesel will be accumulated as the top layer and glycerol will be the bottom layer of the product due to biodiesel having lower density compared to glycerol.

3.2 Biodiesel production from different calcination time of catalyst

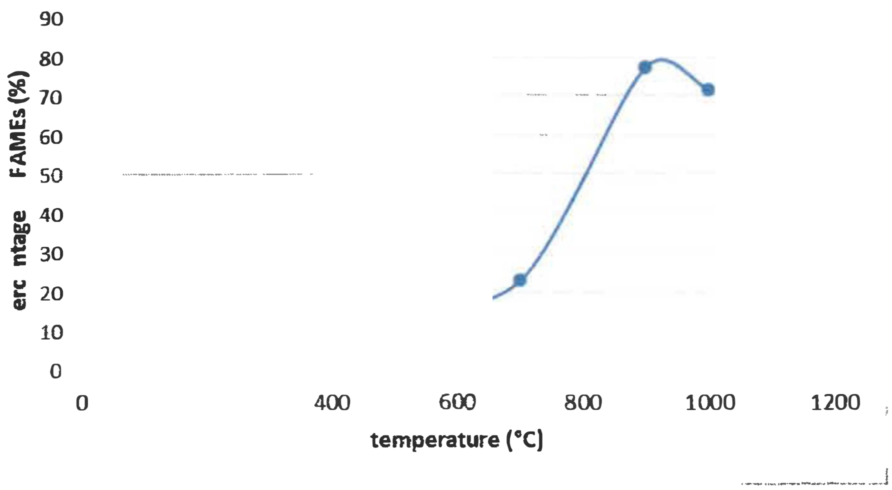

Figure 2: Performance of egg-seashells catalyst for 1.5 hours of calcination time

Figure 2 shows the performance of egg-seashells catalyst that was calcined at different temperature for 1.5 h. At 400°C resulted the lowest percentage of 14.3% biodiesel and at 900°C shows the highest percentage of 77.1% biodiesel that produced in the transesterification process. At temperature 400°C to 700°C, the catalyst is less efficient leads to produce a low yield of biodiesel product. The time proposed in calcination process of egg-seashells catalyst had affected the performance of the catalyst during the reaction. The catalyst was not fully converted into CaO due to the presence of hydroxide sites in uncalcined CaO (Boey et al., 2011). The egg-seashells catalyst needs a longer duration of calcination process to fully convert into CaO particles. The presence of hydroxide sites was identified by the presence of dark colour on the catalyst after calcination process is done. Next, a low percentage of biodiesel is obtained at 1000°C compared to 900°C. The factor that contribute to this result is a shorter reaction time for transesterification reaction, but the temperature proposed for calcination had fulfil the hydroxide sites to fully converted into CaO particles due to less presence of dark colour on the catalyst after calcination.

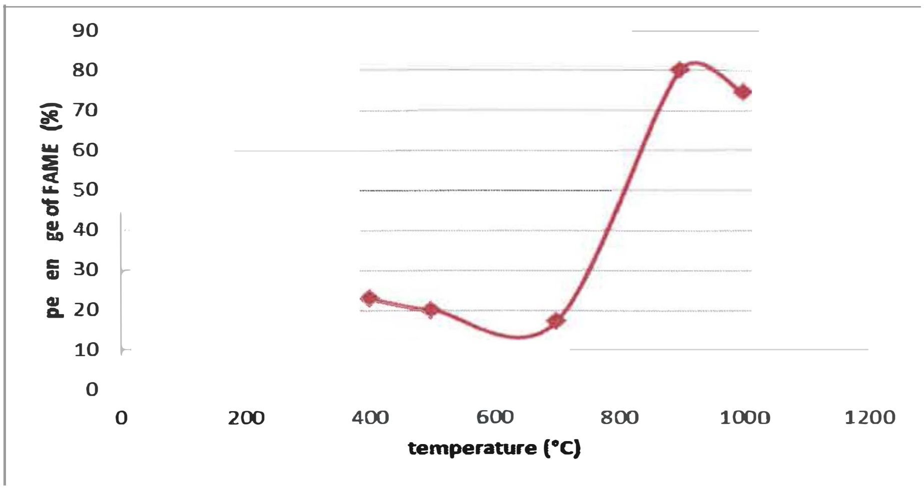

Figure 3: Performance of egg-seashells catalyst for 2.5 hours of calcination time