Utilizing Sabang sea urchin shell as an inexpensive and alternative heterogeneous catalyst for biodiesel synthesis

Z Hayati, M Ramli1, R Mitaphonna, Y Nadia, S Lubis and Amraini
Chemistry Department, Universitas Syiah Kuala, Banda Aceh, Indonesia, 23111
E-mail: muliadiramli@unsyiah.ac.id

Abstract. This research is focused on the utilization of sea urchin shells collected from Sabang island, Aceh, Indonesia as raw material for heterogeneous catalyst preparation and its catalytic study on transesterification reaction of palm oil and methanol to produce fatty acid methyl esters which referred as biodiesel compound. The catalyst was prepared through thermal decomposition method, namely, it was calcined at 900°C in air atmosphere for 4 h and modified with various concentration of potassium element (5, 10, and 20 wt.%) as dopant substance using impregnation process. The characterization results using X-Ray Diffraction (XRD) proved that the produced catalyst was dominated by CaO crystals, in which MgO was detected as a minor compound. Another characterization using Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) showed that the produced catalyst has been homogeneous formation on their morphology. Finally, in order to have scientific information regarding its catalytic activity, the prepared catalyst was successfully applied to the transesterification reaction of palm oil and methanol resulting in ricinoleic methyl esters as the main biodiesel product.

1. Introduction
Sea urchin shell which also referred as Pig Bristles by local people in Indonesia is a kind of marine biota which lives in the coral ecosystem. The spread of sea urchin shell depends on the development of the substrate and food, whereas mostly found in the tidal area of 10 m at depth [1]. Generally, there is only the gonad part of the sea urchin shell used, so that the gonad of sea urchin shell has been noticed as natural protein resource as it has been consumed widely by people in Japan.

Sabang island is one of the famous tourist destination located at westernized Sumatra. Unfortunately, there are many sea urchin shells live in Sabang seashore area, so that is disadvantages for tourism activity. As it reported [3] sea urchin shells live in Sabang seashore area, so that is disadvantages for tourism activity. As it reported [3] sea urchin shells consist of its gonad yields around 2-6%, while more than 90% is shell material. As a fact, the sea urchin shell is still considered as a marine biological waste and its still not utilized optimally. It has been well known that some of the solid wastes such as mollusc, eggshell, fish shell could be used as raw material for heterogeneous catalyst preparation [4]. On the other hand, as its reported by [2], the sea urchin shells composition consist of calcium of 56.23, magnesium of 39.97, sodium of 2.52, and manganese of 0.31 (wt.%).

In order to overcome lack of energy resources based on fossil sources and also to keep the energy sustainability for world population in future, several scientific works have been conducted since several years ago by employing renewable materials such as fatty acid compounds produced by animal

1 To whom any correspondence should be addressed.
and plant for the green renewable, clean and biodegradable energy resources [5]. Therefore, it provides an alternative renewable energy resource, we propose this research work, particularly by utilizing sea urchin shells collected in Sabang seashore area, Aceh–Indonesia as green and inexpensive inorganic material for heterogeneous catalyst matrix and its application study for biodiesel synthesis from palm oil

2. Experimental procedure

2.1. Tools and materials
There are several tools used in this experiment including ceramic mortar, reflux, three-neck squash, hot plate, magnetic stirrer, metal sieve (100 mesh), furnace, separating funnels and some of analytical equipment such as, X-ray Diffraction (XRD) Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) and Gas Chromatography-Mass Spectroscopy (GC-MS). The materials used in the experiment were sea urchin shells, palm oil, methanol, demineralization water, KNO$_3$ 0.1 N, KOH 0.1 N, and phenolphthalein as indicators.

2.2. Catalyst preparation from sea urchin shells
Sea urchins shells used in this experiment were collected from the Iboih seashore area in Sabang island, Aceh-Indonesia. Firstly, the gonad was removed from the sea urchin shells, and then the sea urchin shells washed for removing any organic impurities attached on the shells surface. Then, the shell material was dried under sunlight for half day. Further treatment, the dried sea urchin shells were grained using ceramic mortar and bowl changed to powder particle. The particle sizes were homogenized through sieving process with 100 mesh sieves (150 μm), and continuing by calcination process at 900°C for 4 h in an air atmosphere. The product of calcined powder was classified into two separated bottles. As a comparison study, one group of the calcined sea urchin shells was modified with KNO$_3$ by wet impregnation method with a various potassium concentration of 5, 10 dan 20 (wt.%), and finally, the modified product was recalcined at 550°C for 5 h. The characterization process using XRD and SEM-EDS were carried out for both group of catalyst sample, the originally calcined and modified sea urchin shells catalyst, respectively.

2.3. Physicochemical analysis of palm oil
To evaluate the initial quality of the raw palm oil that used as natural feedstock in this experiment, the physicochemical properties of the palm oil was determined by using scientific procedure, including acid number, density, viscosity, and water content.

2.4. Transesterification of palm oil using sea urchin shells catalyst
To remove any impurities and water content in the raw palm oil, the oil was heated at 105°C for 30 min. Then, methanol and the prepared catalyst material (calcined and modified sea urchin shell) was mixture and heating at 60°C for 10 min by keeping it constant stirring of 600 rpm. The transesterification product was cooled down at room temperature and then filtered to separate to liquid product and catalyst material. The liquid phase transferred to a separated funnel, whereas the top layer of liquid is noticed as methyl ester compound which separated from glycerol at the bottom layer of the liquid [6]. At the final step, the liquid phase of the biodiesel product which existing on the top layer in the separated funnel was taken out for physicochemical evaluation and GC-MS analysis.

3. Results and discussion

3.1. Catalyst preparation
Figure 1. showed the obtained catalyst produced in this experiment with labelled as; (a) uncalcined and, (b) calcined of sea urchin shells catalyst which their particle size of 150 μm. It can be seen that the calcination process on the sea urchin powder has changed its original color (brown) to white,
which could be noted that the calcination process was removing some of the chemical compounds (water and organic compounds) [7].

**Figure 1.** (a) Uncalcined powder (150 μm) of sea urchin shells and (b) calcined powder of sea urchin shells (150 μm, 900°C, 4 h).

### 3.2. Catalyst characterization

In order to evaluate the phase of sea urchin shells crystal obtained in this experiment, the prepared inorganic material which noticed as uncalcined and calcined of sea urchin shells catalysts were characterized using XRD and SEM-EDS equipment. As it can be seen in Figure 3, the introduction of potassium on calcined sea urchin shells particles was increasing the crystallization phase of calcium oxide (CaO) particles in the shell matrix. Based on the XRD pattern as shown in Figure 2(a), the sharp and strong intensity of diffractogram was clearly detected at diffraction angles (2θ) of 32.453°, 37.595° and 54.100° as the specific diffractogram from CaO phases, where is in line with The joint Committee on Powder Diffraction Standards (JCPDS) number 96-101-1096. The positive effect of potassium dopant on increasing CaO crystals in sea urchin shells matrix also supported by Energy Dispersive Spectroscopy (EDS) data resulted in this experiment. Based on the EDS data, it could be meant that the concentration of potassium (K) affecting on assisting of CaO phases on the calcined sea urchin shells, whereas the suitable concentration of potassium dopant was 5 (wt.%). Which contrary while introducing higher concentration of potassium 10 and 20 (wt.%) in which decreasing the formation of CaO phases in the sea urchin matrix.

**Figure 2.** XRD Diffractogram of: (a) Calcined sea urchin shells (150 μm, 900°C, 4 h) and (b) modified sea urchin shells with potassium 5 wt.%.
Figure 3 showed the SEM images of the calcined sea urchin shells (150 μm, 900°C, 4 h) and modified sea urchin shells with potassium 5 wt.% resulted in this experiment. It can be observed that the impregnation of potassium as the dopant substance on the surface of sea urchin shells changed the sea urchin shells morphology as a result of physical interaction between sea urchin shells material and potassium dopant. It can be illustrated that during the impregnation process, the KNO3 compound attacks on the pore of sea urchin material. Further heating treatment (at 550°C) on the modified sea urchin shells assisted the modification process as shown in Figure 3.

![Figure 3. (a) Calcined sea urchin shells (150 μm, 900°C, 4 h), and (b) modified sea urchin shells with potassium 5 wt.%](image)

Evaluation the chemical composition of the calcined sea urchin shells and the modified sea urchin shells with potassium 5 wt.% samples were carried out using EDS as shown in Table 1, which can be understood that the impregnation of potassium on sea urchin shell matrix was increased CaO crystal to 34.03 wt.%

### Table 1. The result of EDS analysis of unimpregnated sea urchin shells and impregnated sea urchin shells with KNO3 5 wt.%.

| Element | Unimpregnated sea urchin shells | Impregnated sea urchin shells with potassium (KNO₃) 5 wt.% |
|---------|---------------------------------|----------------------------------------------------------|
| O K     | 38.72                           | 42.06                                                    |
| Mg K    | 7.83                            | 2.15                                                     |
| Al K    | 1.13                            | -                                                        |
| Si K    | 8.09                            | -                                                        |
| Cl K    | 1.07                            | 0.46                                                     |
| Ca K    | 31.44                           | 34.03                                                    |
| Fe K    | 2.61                            | -                                                        |
| As L    | 6.54                            | -                                                        |
| C K     | -                               | 26.14                                                    |
| K K     | -                               | 1.43                                                     |
| **Total** | **100**                          | **100**                                                   |

3.3. Catalytic study on transesterification reactions of palm oil

To evaluate of the catalytic activity of the sea urchin shell catalyst which prepared in this experiment, the transesterification reaction using palm oil and methanol was conducted with the experimental condition of 60°C, palm oil-methanol ratio of 1:15, time reaction of 3 h and catalyst weight of 5 wt.%. Figure 4 showed the liquid product produced in the transesterification process. It is clearly seen that the two layers of liquid had been formed after left for 24 h in room temperature. The upper layer was
indicated as crude biodiesel, while the lower layer was glycerol mixed with remaining methanol and unseparated catalyst. The upper layer was separated for taking physicochemical and GC-MS analysis to have qualitative information the product.

**Figure 4.** Liquid phase produced by transesterification reaction of palm oil and methanol using (a) unimpregnated sea urchin shells catalyst and (b) modified sea urchin shells catalyst with potassium of 5 wt.%.

3.4. Analysis of the synthesized biodiesel using GC-MS
The qualitative composition of produced biodiesel was evaluated using GC-MS as is presented in Table 2. The identification of GC-MS chromatogram confirmed that the palm oil successfully converted into methyl ester compound. As its summary on Table 2, in which three main compounds are methyl palmitate (14.01%), methyl oleate (13.86%), and methyl ricinoleic (56.78%) as the main substance in the biodiesel product.

| Peak number | Retention time (R) | Peak area (%) | Compound              |
|-------------|--------------------|---------------|-----------------------|
| 1           | 20.393             | 14.01         | Methyl palmitate      |
| 2           | 24.278             | 13.24         | Methyl oktadecadienate|
| 3           | 24.508             | 13.86         | Methyl oleic          |
| 4           | 25.225             | 2.11          | Methyl stearate       |
| 5           | 28.551             | 56.78         | Methyl ricinoleic     |

4. Conclusion
This research work confirmed that the inorganic heterogeneous catalyst was successfully prepared from sea urchin shell collected from Sabang Island in Aceh. The impregnation of potassium on the has been assisted inorganic crystalline growth contained in the calcined sea urchin shell material. The inorganic catalyst produced from the sea urchin shell proved their catalytic activity on transesterification reaction of palm oil with methanol to produce methyl esters, as biodiesel compound.

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