Transesterification of Pangium Edule Reinw oil to biodiesel using durian rind ash as heterogeneous catalysts

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Abstract. The purpose of this research is to know the effect of addition durian rind ash as a catalyst for biodiesel production. Waste of Durian rind ash containing potassium oxide compound can be used as a novel heterogeneous catalyst for the transesterification process. Potassium oxide in durian rind ash catalyst has been synthesized by the simple burning method. In this research, durian rind ash catalyst was potentially for biodiesel production from Pangi (Pangium Edule Reinw) oil. The optimum biodiesel yield of 96.24% can be achieved over durian rind ash catalyst of 5 wt.% of catalyst, reaction temperature 65°C at 1 hour, and a methanol-to-Pangi oil ratio of 8:1. The characterization was also conducted using X-ray diffraction (XRD) and Scanning electron microscopy (SEM).

1. Introduction
Nowadays fossil fuels are depleting. Great efforts have been done in developing processes for biodiesel generating from renewable sources [1,2]. The first generation biodiesel as an alternative fuel is a renewable fuel with superior process and emissions compared to commercial diesel. Biodiesel has ecological impacts related to potentially sustainable and clean energy for a better future. Indonesia has also participated to produce biodiesel as a motivation to utilize clean energy from emissions of fossil-based energy [3]. Biodiesel which is also known as fatty acid methyl ester (FAME) is generally obtained through the transesterification reaction of vegetable oils or animal fats. This reaction is given by several factors such as alcohol molar ratio to oil, reaction time, reaction temperature, catalyst concentration, stirring speed and water content and free fatty acid content (FFA) [4]. Pangi oil (Pangium Edule Reinw) is a type of vegetable oil that potentially converted into biodiesel with an amount of oil weight of 20% of its dry weight. The highest fatty acids composition in Pangi oils are oleic acid and linoleic acid namely 45.2% and 39.3%, respectively [5].

The transesterification reaction is inseparable from the role of the catalyst as a substance that acts to accelerate the reaction. The use of heterogeneous catalysts is now preferred to be developed because it has various advantages over homogeneous catalyst and enzymes such as cheap, easily separated, non-corrosive and reusable [6]. Several types of heterogeneous catalysts used for the production of biodiesel
are zeolite, alkali metals, and the most developed are types of alkaline earth metal oxides [7]. This type of metal oxide catalyst is known to be more active to produce non-toxic products. This catalyst can be obtained from sludges, slags and also ash through thermal treatment above 1200°C [8]. Bennett et al [9] also explain that heterogeneous base catalysts provide a more significant conversion than acid heterogeneous catalysts. Several types of solid catalysts are sourced from several biomass treatments such as snails, eggs, cockle, coconut fiber, oil palm empty fruit bunches and so on [10]. This is closely related to the conservation of natural resources, especially for materials that can rarely be reused. Durian (Duriozibethinus murr) is a plant that grows in Southeast Asian countries such as Indonesia, Philippines, and Malaysia. Lubis et al [11] said that 900,000 tons per year of durian production starting in the next 20 years. Durian has a diameter of about 80 cm. The colour of this fruit is generally green, brownish-green, yellowish-green and yellow. Its rind also rough and has conical spines [12]. Durian fruit consists of 20-30% fruit flesh, 5-15% seeds, and 60-70% rind [13].

In reality, durian rind is produced from durian fruit consumption because the consumed part of the durian is only the flesh, meanwhile, its seeds and rinds are thrown away. The existence of durian rind waste is also disturbing because it has a distinctive aroma that many people do not like [14]. Increased durian production has an effect on increasing durian rind waste. Durian rind is usually reprocessed into adsorbents, pulping and biodegradable films [15-16]. The chemical components of durian rind are P₂O₅, MgO, CaO, SiO₂, Fe₂O₃, SO₃, Na₂O, Al₂O₃, MnO and K₂O as the largest components [13]. The high content of potassium oxide suggests an active phase for a certain reaction. In addition, the results of the proximate analysis also showed that the content of durian rind ash contained was 0.4% of the dry basis [17]. The purpose of this study is to investigate the effect of the ratio of methanol to Pangi oil using a durian skin ash catalyst. The morphology and the composition of the catalyst are also identified by SEM and XRD.

2. Methodology

2.1 Materials

The durian ash catalyst was prepared from durian rind including inner skin collected from markets around the city of Banda Aceh, Indonesia. Methanol was purchased from Merck (99.5%), Darmstadt, Germany. Pangii oil was purchased from traditional farmers in the region of Calang Aceh Jaya, Indonesia.

2.2 Catalyst Preparation

Durian rind waste was dried at 32°C. The preparation was then continued by size reduction through cutting then crushed using a mechanical crusher. The sample was then burned in the open air to obtain durian rind ash.

2.3 Catalyst Characterizations

The structural of the samples of durian rind ash were investigated using powder X-ray diffraction (XRD, Shimadzu XRD-6000), having Cu K alpha radiation with 40 kV and 40 mA at scanning rate of 10/min, sampling width 0.02. The morphology of durian rind ash catalyst was characterized using a Scanning Electron Microscopy (SEM, Philips XL-30) apparatus.

2.4 Transesterification of Pangii oil

About 30 grams of (Pangium Edule Reinw) oil is put into a three-neck flask. Then methanol was added with volume corresponds to the varied mole ratio of methanol to Pangii oil. Durian rind ash catalyst was added at a constant loading of 5wt.% to oil. The process was carried out with stirring at a constant temperature of 65°C for 60 minutes. After the process was completed, the product was separated using a separating funnel and continued with washing using warm water. The yield of biodiesel was then calculated using equation (1).

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\text{%Yield} = \frac{\text{Weight of biodiesel produced}}{\text{weight of oil used}} \times 100\% 
\]
3. Result and discussion

3.1 Characterization of durian rind ash catalyst
A scanning electron microscopy (SEM) image shows that the durian rind ash catalyst has a hollow and irregular morphology. This is one of the effects of the non-uniform distribution of elements. Durian rind ash catalyst also has a micro-size pore ranging of 1-2.6 μm and mesopore with an approximate size of ± 3.7 μm.

![Figure 1. SEM image of durian rind ash catalyst](image)

Pore size with the large specific surface area can facilitate the efficiency of reactant contact and its accessibility to active sites [18]. Durian rind ash is also seen to agglomerate as a result of particle interactions during the combustion process [19]. In addition, the wide surface area of the catalyst can also affect the mechanical stability of the durian rind ash catalyst [9].

![Figure 2. XRD analysis of the durian rind ash catalyst](image)

3.2 XRD Analysis
The XRD pattern of the durian skin ash catalyst is shown in Figure 2. X-ray diffraction methodology was done to evaluate the composition of durian rind ash. XRD spectrum of durian rind ash can be seen in Figure 2.
Figure 2 reveals that the potassium oxide is the highest component of the catalyst as marked by the appearance of the highest peak with prominent 2θ at 29,680°, 27,896°, 40,576°, 42,893°, and 62,250°. Potassium oxide is one of the active components that work effectively in the transesterification reaction [20]. Husin et al. also stated that potassium has good catalytic activity and regeneration ability. Potassium can play a role in increasing anion methoxide to break the carbon carbonyl bonds of triglycerides informing biodiesel (Methyl ester) [21].

3.3 Effect of methanol to oil molar ratio on yield
The stoichiometry of the transesterification reaction shows that one mole of biodiesel requires 3 moles of alcohol. The reversible nature of the reaction results in the transfer of excess alcohol to the product side [22]. Therefore, a higher molar ratio can be applied to increase miscibility and contact between alcohol molecules with triglycerides [23]. This investigation is needed to minimize the use of methanol in the transesterification reaction. In this study, variations in the molar ratio of methanol to Pangi oil were carried out in 4:1, 6:1, 8:1, 10:1, 12:1, and 15:1. The yield obtained is as presented in Fig. 3.

![Figure 3. Effect of methanol to pangi oil molar ratio (65°C and catalyst 5 wt.%)](image)

Fig. 3 showed that the transesterification reaction with methanol to oil molar ratio variations of 4:1, 6:1 and 8:1 brings about the increment in biodiesel yield. Those are 93.64, 95.98, and 96.21% respectively. For these high yield shows the process of Pangium Edule Reinw oil to biodiesel is in a stable polarity so the solubility of glycerol to return become ester phase can be reduced [24]. However, biodiesel yield slightly decrease from 10:1, 12:1 and 15:1 of molar ratio of methanol to oil. It seems, the decreasing of biodiesel yield due to difficulty of product separation from the glycerol layer when the methanol to oil ratio increase. This phenomenon is also reported by other research groups [25]. This acquisition between the two mole ratio variations requires further study related to the role of the diesel fraction as a major component [26].

4. Conclusion
The heterogeneous catalyst from durian rind ash has been applied for the transesterification reaction of Pangi oil prepared through a simple combustion method and successfully produced biodiesel with a high yield of 96.21% using 5% catalyst loading at 65°C for 1 hour with 8:1 mole ratio of methanol to oil. The combustion process increased the catalytic activity and mechanical stability of the durian rind ash.
catalyst. Durian skin ash contains potassium oxide which owns good ability and stability makes it has the potential to be utilized as a material for catalyst biodiesel production.

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6. References
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