Concentration of CaO catalyst from chicken eggshell in transesterification process of pangi seed oil biodiesel

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Abstract. The purpose of this research was to obtain best concentration of CaO catalyst chicken eggshell in transesterification process of pangi seed oil biodiesel. The treatment of CaO catalyst concentrations in this research was S1 (1%), S2 (1.5%), S3 (2%), S4 (2.5%), and S5 (3%). The collected data were statistically analyzed by using Analysis of Variance (ANOVA) continued by Duncan’s New Multiple Range Test (DNMRT) test at 5% level. The parameters observed were acid value, density, iodium value, saponification value, and cetana number. The results of analysis showed that concentration of CaO catalyst chicken eggshell gave unsignificantly affect on acid value and cetana number but significantly affect on density, iodium value, and saponification value of biodiesel. The chosen treatment in this research was S5 (CaO catalyst 3%). The treatment of S5 has yield 97.99% with characteristics acid value 0.68 mg KOH/g, density 885.22 kg/m3, iodium value 81.41 g I2/100 g, saponification value 179.00 mg KOH/g, and cetana number 58.48.

1. Introduction
Indonesia is one of the world’s most populous country. The big number of population makes the increasing needs of energy. In Indonesia, the energy source is still depending on petroleum fuel, which is reduced days-by-days as it is not renewable. The usage of refined petroleum products always increases every year and in-line with its usage in industry, transportation, and diesel power plants (PLTD) in various regions.

Several ways to suppress the growth of fuel consumption which have been done are to make regulations on energy saving and also to develop the alternative energy. One of the renewable alternative energy that has the potential to solve the fuel problem is biodiesel.

Biodiesel is a renewable fuel consisting of a mixture of mono alkyl esters of long-chain fatty-acids. Biodiesel is a promising alternative fuel that can be obtained from plants and animals or used oil through transamidation with alcohol [10]. However, the current alternative energy source still mostly comes from Crude Palm Oil (CPO) raw materials. This will interfere to the needs of food since one of CPO’s source is the vegetable oil from food substance. This begins as the background research to search for alternative energy sources materials that is not from food’s substance, one of them is pangi (Pangium edule Reinw.).

Pangi is a plant that is easy to grow in the tropical climate. Indonesia is a tropical area and suitable for the growth of pangi plant. The wild-growing pangi plant is easily found in Riau - precisely in the village of Tanjung Belit Selatan, Kampar Kiri district, Kampar regency. Pangi plants unevenly
spreading in the village of Tanjung Belit Selatan, so the number of plants and the area of land planted with this plant is difficult to record in detail.

In general, biodiesel production uses homogeneous catalysts such as NaOH and KOH. The conversion achieved using a homogeneous catalyst is about 98%, which is considered very high. However, the weakness of the homogeneous catalysts is that it is difficult to separate the dissolved catalyst from the desired product. It resulted to the less economical production process. Therefore a biocatalyst heterogeneous catalyst is required such as the use of CaO catalyst.

Chicken eggshell contains 94% CaCO3 (calcium carbonate), 1% MgCO3 (magnesium carbonate), 1% Ca3 (PO4)2 (calcium phosphate), and 4% of other organic ingredients [17]. To make CaO catalyst from chicken eggshell, firstly we calcined the eggshell to obtain a good CaO catalyst. Calcination is the process of eliminating CO2 compounds found in chicken eggs to form CaO. The calcination temperature used should be above 800°C [21]. Based on [21], the value of biodiesel yield produced using raw material of soybean oil with CaO catalyst from chicken eggshell is above 95%.

In this research, the biodiesel was made from pangi seed oil through transesterification process using CaO catalyst from chicken eggshell that has been calcinated at 900°C. The purpose of this study was to obtain the best concentration of CaO catalyst from chicken eggshell in transesterification process to get the best quality of biodiesel produced from pangi seed oil.

2. Material and Methods

2.1. Time and Location
This research has been conducted in Laboratory of Agricultural Product Analysis Faculty of Agriculture and Laboratory of Organic Chemistry and Natural Material Faculty of Mathematics and Natural Sciences University of Riau. The study lasted six months from April to October 2017.

2.2. Tools and Materials
The main ingredients used are oil from pangi seed obtained in the Village of Tanjung Belit Selatan, Kampar Kiri Sub-district Kampar. The eggshells were obtained from fried rice traders in Panam. Other ingredients used are methanol, Na-tiosulfat (Na2S2O3) 0.1 N, paper strain, distilled water, phenolphthalein indicator, 10% KI solution, chloroform, wijs reagent, starch solution, KOH 0.5 N, HCl 0.5 N, and isopropyl alcohol.

The tools used are blast, 250 ml erlenmeyer, magnetic stirer, oven, 100 mesh sieve, mortal, condenser, hot plate stirrer, bucket, hose, thermometer, analytical scales, dropper, measuring cylinder, buret, separating funnel, statip, pumpkin neck three, porcelain cup, piknometer, tissue, stationery, and camera.

2.3. Research Method
The research was conducted by using Randomized Complete Random Design which consist of five treatments, namely S1 (CaO Catalyst1% and 99% pangi seed oil), S2 (CaO catalyst 1.5% and 98.5% pangi seed oil), S3 (CaO catalyst 2% and 98% pangi seed oil), S4 (CaO catalyst 2.5% and 97.5% pangi seed oil), and S5 (CaO catalyst 3% and 97% pangi seed oil).

2.4. Research Implementation Pangi Seed Oil
Pangi Seed oil extraction is done by taking the seed of ripe pangi fruit, discarded its shell, and soaked it with running water for 24 hours. The seed then dried by oven at 70°C for 24 hours. It was then pressed until the extract come out. The oil was then filtered with filter paper, then its water content and free fatty acids were analyzed.

2.5. CaO Catalyst Preparation from Chicken Eggshell
The eggshell was crushed with a mortal or blender and sieved with an 80 mesh sieve to get homogeneous size. It was then washed with water to remove impurities such as dust attached.
2.8. Biodiesel Purification

The purification process is needed to remove water that may still be left in biodiesel. Purification of biodiesel is done by heating at 105°C for 20 minutes [20].

2.10. Data Analysis

Data obtained from analysis of acid number, density, iodine number, saponification number, and cetane number will be analyzed statistically using Analysis of Variance (ANOVA). If the results obtained was $F_{\text{counted}} \geq F_{\text{table}}$, it will be tested further by using Duncan’s New Multiple Range Test (DNMRT) at 5% level.

3. Results And Discussion

3.1. Panggi Seed Extraction

The extract of dried panggi seed contained 12.73% panggi oil. The results of calculation of oil panggi yield can be seen in Appendix 6. The low oil yield produced in this research was caused by traditional tool of its press tool (alat kempa), so the extract result is not maximum.

3.2. Raw Material Analysis

3.2.1. Water Content. The panggi oil resulted has 0.044% water content. According to [13] the maximum requirement of water content to be used as raw material for biodiesel in oil is 1%. Based on the analysis of water content that has been done, the water content of the resulting panggi oil meets the requirements of raw materials to be used as biodiesel.
3.3. Free Fatty Acids
Pangi seed oil produced has a high fatty acid content of 1.73%. [7] States that the presence of free fatty acids present in oils less than 5% will not interfere with the transesterification process if using a heterogeneous base catalyst in the transesterification process. Based on the analysis of free fatty acids that have been done, pangi is qualified to be used as biodiesel raw materials.

The quality of biodiesel is determined by the raw materials used. Free fatty acids and water content are two important factors in biodiesel raw material. Based on the analysis, Pangi’s oil and d free fatty acid content in this research have fulfilled the requirement of raw material for biodiesel production, so that transesterification process can be done immediately without any preliminary treatment.

3.4. Transesterification Reaction Result
Variations of CaO catalysts used in the transesterification reaction were 1%, 1.5%, 2%, 2.5%, and 3% of the material weight. The biodiesel yield in transesterification reaction can be seen in Figure 1.

![Figure 1. Effect of catalyst CaO concentration on yield biodiesel](image)

Based on Figure 1. The higher the CaO catalyst concentrate used, the higher yield of biodiesel produced. The resulting yield increase is due to the transesterification reaction in which the use of the catalyst serves as a speeding reaction rate so that the oil reacts more quickly with methanol to produce methyl esters. This is consistent with research by [14] which states that the higher the number of basic catalysts used, the higher the yield of biodiesel produced.

3.5. Biodiesel Characteristic
3.5.1. Acid Number. Acid number is one indicator that plays an important role in biodiesel. Acid numbers can determine the possible extent of damage during biodiesel storage. The result of variance analysis showed that the addition of CaO catalyst at different concentrates had no significant effect on the number of biodiesel acid produced. The average value of the biodiesel acid number can be seen in Figure 2.
Figure 2. Effect of catalyst CaO concentration on acid number

The higher the catalyst concentrate used, the lower the resulting biodiesel acid number. The low acid number of biodiesel produced is because the number of fatty acid content of the pangi oil was not too high to be used as raw material for making biodiesel. The other reason is because the catalyst used in this biodiesel transesterification reaction is the base catalyst, so that the free fatty acids present in the oil will react with the base catalyst used.

Acid numbers can be used to determine the level of corrosivity of biodiesel produced. According to [8] the smaller the acid number, the better quality biodiesel produced because the level of corrosivity will also be smaller. The maximum number of biodiesel acid number according to SNI is 0.8 mg KOH/g. The results obtained in this study have met the SNI biodiesel standards of 0.68 - 0.71 mg KOH/g.

3.6. Density
Density is the ratio between the weight of an oil or fat sample volume at a certain temperature compare to the weight of water at the same temperature and volume. The weight of the oil or fat is influenced by the unsaturation degree and the average molecular weight of the fatty acids component of oils or fats, since fatty acids are the largest components contained in oils or fats. The average weight value of biodiesel type can be seen in Figure 3.

Figure 3 shows the average density of biodiesel produced was 885.23-889.37 kg / m³. The densities of S1, S2, S3, S4, and S5 treatments was significantly different. The larger the CaO catalyst concentrations used in the production of biodiesel, the less biodiesel was being produced. This might occurred because in the transesterification reaction, the oil reacts with methanol perfectly so that the oil is converted to methyl esters. According to [15] the density is one indicator of the presence or absence of impurities such as soap and glycerol that do not react with methanol.

The density is related to the heat and power generated by the diesel engine. Low density will produce high heating value whereas biodiesel with density exceeding standard will cause incomplete combustion reaction in biodiesel [2]. Biodiesel with this quality is not used in diesel engines because it can increase engine wear and emissions and cause damage to the engine [5]. The biodiesel density according to SNI is 850-890 kg / m³. The results obtained in this study have met the SNI biodiesel standard that is 885.23-889.37 kg / m³.
3.7. Iodine Number
The iodine number indicates the unsaturation of the fatty acids contained in the biodiesel. Unsaturated fatty acids can bind to iodides and form saturated compounds. The number of tied iodides shows the number of double bonds. The average biodiesel iodine value can be seen in Figure 4.

Figure 4. Shows that the average number of iodine biodiesel produced ranges from 81.41-89.60 mg/g. The higher the catalyst concentrate used, the smaller the iodine number. This is likely to occur due to the disconnection of the double bond in biodiesel during the transesterification reaction and also the high temperature used when drying the. This is consisten [16] research which states that the decline in the iodine number of mahogany seed oil is caused because of some double bonds are broken in the purification process due to heating, air, and chemical processes.

The iodine number shows the number of double bonds in the biodiesel fatty acids. Unsaturated fatty acid compounds can improve the performance of biodiesel at low temperatures, because it has lower melting point [10]. High iodine number in biodiesel can cause blockage of injection lines in diesel engines due to instability unsaturated fatty acids caused by high temperature. It can form deposits and easily react with oxygen in the atmosphere and can be polymerized to form similar
materials of plastic [1]. The results obtained in this study have met the SNI standard of biodiesel that is equal to 81.41-89.60.

3.8. Saponification Number
The saponification number is the amount of alkali required to soaps a number of biodiesel samples. The amount of saponification depends on the weight of the molecule. The average value of the biodiesel saponification number can be seen in Figure 5.

![Figure 5. Effect of catalyst concentration on saponification number](image)

Figure 5. shows that the average saponification number of biodiesel produced ranges from 163.39-179.00 mg KOH/g. The higher the concentration of catalyst used, the greater the saponification number generated. This is because in the transesterification reaction there is a saponification reaction between the CaO catalyst and the oil that causes the breakdown of the carbon chain in the oil which results in the reduction of the molecular weight of the oil so that the number of saponification increases.

Oil weight is associated with the length of the carbon chain in the fatty acid contained in the triglyceride and will affect the amount of KOH required to soaps the oil. According to [11] oils or fats composed by short-chain fatty acids mean that they have a low molecular weight or density which has a relatively high saponification number.

The saponification number is closely related to the density of the biodiesel obtained. According to [9] the density of the biodiesel depends on the saponification number. Oils with low density will have higher saponification number rather than oils with high density.

The use of base catalyst will increase the tendency of saponification reaction between the alkali metal and the catalyst used [12]. Oils or fats are reacted with excess alkali in the alcohol. The alkali will react with triglycerides to form soap. Less amount of catalysts used will cause the transesterification reaction not to run optimally so that the biodiesel yield obtained is also reduced.

The biodiesel saponification number obtained in this study was 163.39-179.00 mgKOH/g. Biodiesel’s SNI saponification is not yet determined, but the smaller the saponification number obtained, the resulting biodiesel will improve in the combustion process in the diesel engine used. The saponification number in this study is used to calculate biodiesel cetane number.

3.9. Cetane Number
Cetane numbers show how quickly the fuel of diesel engines injected into the combustion chamber can burn spontaneously after mixing with air. The higher the fuel cetane number, the faster a diesel engine burns after it is injected into the combustion chamber [10]. The average number of this research’s biodiesel cetane number can be seen in Figure 6.
Figure 6. shows that the average cetane number of biodiesel produced is 58.47-59.54. The more catalysts used, the lower the cetane number will be. This might be because catalyst can accelerate the reaction process so that in the transesterification reaction, it also accelerated the oxidation reaction that causes the formation of double bonds on the fatty acid oil chain. According to [19] biodiesel containing high saturated fatty acids will have high cetane numbers, whereas those containing one-bond fatty acids have medium cetane numbers and those containing double bonned fatty acids with double bond or more have low cetane numbers.

The length of the hydrocarbon chains present in fatty acids causes a high rate of cetane biodiesel as compared to diesel [10]. Cetane numbers in diesel fuel indicate the quality of fuel ignition, which indicates the readiness of diesel engine fuel to ignite spontaneously at certain temperature and pressured conditions in the combustion chamber. The higher the fuel cetane number, the delay time between injection and ignition is shorter and the quality of lighting is better.

The cetane number in this pangi seed oil biodiesel production research ranges from 58.47-59.54, while SNI biodiesel standard for cetate number is at least 51. So, biodiesel from pangi seed oil meets SNI standard.

3.10. Recapitulation of Best Treatment Analysis Results

Based on the observed parameters (acid number, density, saponification number, iodine number, and cetane number), the biodiesel with best treatment have been selected. The results recapitulation for all treatments analyses are presented in table 1.

<table>
<thead>
<tr>
<th>Analysys</th>
<th>SNI</th>
<th>Treatment</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Number (mg KOH/g)</td>
<td>&lt; 0.8</td>
<td>0.711</td>
<td>0.705</td>
<td>0.702</td>
<td>0.688</td>
<td>0.682</td>
<td></td>
</tr>
<tr>
<td>Density kg/m³</td>
<td>850-890</td>
<td>889.37</td>
<td>888.71</td>
<td>887.88</td>
<td>886.41</td>
<td>885.22</td>
<td></td>
</tr>
<tr>
<td>Iodine Number g I₂/100g)</td>
<td>Max 115</td>
<td>89.601</td>
<td>88.855</td>
<td>85.145</td>
<td>82.111</td>
<td>81.414</td>
<td></td>
</tr>
<tr>
<td>Saponification Number (mg KOH/g)</td>
<td>-</td>
<td>163.39</td>
<td>164.69</td>
<td>169.29</td>
<td>174.17</td>
<td>179.00</td>
<td></td>
</tr>
<tr>
<td>Cetane Number</td>
<td>Min 51</td>
<td>59.544</td>
<td>59.447</td>
<td>59.383</td>
<td>59.162</td>
<td>58.473</td>
<td></td>
</tr>
</tbody>
</table>

Note: The number in bold shows the biodiesel with the best treatment.
The biodiesel best treatment in this research is selected by referring it to SNI 7182: 2006 about quality standard of biodiesel. Data in Table 1. shows that biodiesel with pangi seed raw material with CaO catalyst from chicken eggshell is in S5 treatment (3% CaO catalyst concentrate) which has acid number of 0.68 mg KOH/g, density 885.22 kg/m³, iodine number 81.41 g I₂/100 g, saponification number 179.00 mgKOH/g, and cetane number 58.47.

4. Conclusions And Recommendation

4.1. Conclusions
Differences in CaO catalyst concentration from chicken eggshell have no significant effect on acid numbers and cetane numbers but have significant effect on density, iodine number, and saponification number of produced biodiesel. The best treatment of biodiesel obtained at S5 treatment (3% CaO catalyst) yielded a yield of 97.99%, with biodiesel characteristics of acid number 0.68 mg KOH / g, density 885.22 kg / m³, saponification number 179.00 mg KOH / g, iodine number 81.41 g I₂ / 100g, and the cetane number 58.47. The quality of biodiesel produced meets the biodiesel SNI set by the government and the standard of diesel fuel.

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