Rubber seeds are the waste products of rubber plantations which are abundant in availability but have not been fully utilized. Rubber seed production in Indonesia currently reach 5 million tons per year, with oil content of 40-50% can produce rubber seed oil of 2 million tons per year [1]. Therefore, rubber seed oil has the potential to be developed as a raw material for biodiesel and this process directly reduces environmental waste. However, the main obstacle in the use of rubber seed oil as a raw material in the process of making biodiesel is the high free fatty acid (FFA) content of 5-40%. Conventionally, biodiesel production is by reacting vegetable oil with alcohol using an alkaline catalyst. However, alkaline catalysts only work well in oils with low FFA levels <0.5% and in water-free conditions. For vegetable oils with a high
FFA content, the use of alkaline catalysts can cause a saponification reaction thereby reducing the yield of biodiesel produced.

Research related to the manufacture of biodiesel from rubber seed oil has been carried out with various methods including conventional methods with homogeneous catalysts, supercritical methanol, In situ transesterification and Ultrasound assisted [2-4]. However, the problems that arise are almost the same, including difficulty in the separation process, corrosion problems and the impact of environmental pollution. Moreover, the supercritical method must be carried out at high temperature and pressure so that the process costs are more expensive for tool maintenance [5]. Heterogeneous acid catalysts or solid acid catalysts can be used as a solution in making biodiesel from oil with high FFA content because of their reusability and regeneration, easy separation process, higher reaction rate and selectivity, low cost, less energy requirements, and environmentally friendly [6, 7]. The use of a heterogeneous acid catalyst will not produce soap through the neutralization reaction of free fatty acids or saponification of triglycerides. In addition, by using a heterogeneous acid catalyst the FFA esterification process and triglyceride transesterification can be carried out in one reaction stage so as to reduce production costs [8]. Some of these catalysts are zeolite [9], silica [10] alumina [11], nafion [12], MCM-41 [13], amberlyst-15 [14], and sulfate zirconia [15] are catalysts that can be used in the process of making biodiesel [16]. This catalyst has been used for esterification and transesterification of some vegetable oils. In general, the use of solid acid catalysts shows good performance for the esterification reaction even in vegetable oils with high FFA content. However, basic catalysts such as metal oxides still show higher performance or activity than solid acid catalysts [17]. Several types of solid oxide catalysts that have been used include CaO [18], MgO [19], SrO [20], ZnO [21], PbO [22], and zirconium oxide [23]. Therefore, a combination of a solid acid catalyst such as zeolite coupled with metal oxides will provide a higher conversion of biodiesel products at lower relative temperatures [24]. Heterogeneous catalysts that have both acid and oxide sites can perform esterification of FAA and transesterification of triglycerides simultaneously to produce biodiesel [25]. In addition, zeolite with a higher acidity than silica and alumina produces a stronger interaction with metal oxides so that the catalyst is more stable.

Based on that, this research develop the method of making biodiesel from rubber seed oil using a solid acid catalyst (heterogeneous) based on natural zeolite which is very abundant in Indonesia. Before being used as a natural zeolite catalyst, activation will be carried out to increase its catalytic activity by chemical and physical methods and modification of its acidity by developing ZrO2, ZnO, and PbO metal oxides. The resulting catalysts are expecting to act as a bifunctional catalyst that play the role in the FAA esterification process and triglyceride transesterification at the same time so as to increase the quantity and quality of biodiesel. In addition, reusable heterogeneous catalysts can reduce production costs as well as environmental toxicity. Biodiesel produced from rubber seed oil with heterogeneous catalysts is expected to act as an alternative fuel to substitute for fossil fuels or be part of sustainable energy in the future, thereby reducing the problem of limited resources and environmental pollution.

**Material and Methods**

**Materials**

The materials used in this study were: distilled water, aquabidest, natural zeolite, ZrCl4 (pa Merck), zinc-nitrate and Pb-nitrate (pa Merck), HCl (pa Merck), nitrogen gas, oxygen gas (PTAneka Gas Indonesia), Rubber Seed, N-Hexane (technical), Methanol (pa Merck), NaOH (pa Merck), AgNO3 (pa Merck), Ethanol 96%, Indicator PP.

**Preparation of Rubber Seed Oil**

The process of extracting oil from rubber seeds in this study was carried out by an extraction process. Previously, the preparation of rubber seed samples had been carried out including the steps 1) separating the rubber shells and seeds, 2) drying the rubber seeds in the sun, then 3) manually reducing the size of the rubber seeds, then taking the rubber seed oil using the extraction method in soxhletation using n-hexane solvent.

**Preparation and Activation of Natural Zeolite**

The preparation and activation of natural zeolite in this study followed the procedure reported by Sihombing et al. [26] In the early stages, natural zeolite was crushed and sieved to obtain zeolite with a size of 100 mesh. This natural zeolite was then washed by soaking in distilled water for 24 hours at room temperature. Then the zeolite was filtered and the clean precipitate was dried at a temperature of 100°C to obtain a clean natural zeolite (ZB) sample. The ZB sample was chemically activated with 3M HCl, refluxed at 90°C for 30 minutes then filtered, the resulting sediment was washed with aquadest until the pH was neutral, the precipitate was oven at 120°C to dry for 3 hours, followed by calcined at 500°C with nitrogen gas flow to obtain acid-activated natural zeolite (ZAA).

**Synthesis of ZrO2/ZAA, ZnO/ZAA, and PbO/ZAA Catalysts**

Synthesis of ZrO2/ZAA, ZnO/ZAA, and PbO/ZAA catalysts was was done by wet impregnation method. At the initial stage, a metal precursor solution and ZAA
was made with a certain ratio. Then the two solutions were mixed into a three neck flask and reflux was carried out at 90°C for 4 hours, followed by the filtering process. The precipitate obtained was dried at 130°C followed by a calcination process at 500°C for 1 hour with a nitrogen gas flow, then oxidized at the same temperature with oxygen gas flow for 1 hour to obtain ZrO$_2$/ZAA catalyst. The same procedure was carried out for the preparation of ZnO/ZAA, and PbO/ZAA catalysts. Some of the important physical and chemical characteristics of ZrO$_2$/ZAA, ZnO/ZAA, and PbO/ZAA catalysts were characterized using: XRD, SEM, EDX and nitrogen gas sorption analysis with BET method.

**Results and Discussion**

**Cristallinity Analysis**

Testing the properties of zeolite crystals was carried out by using X-Ray Diffractometer (XRD). The characteristic zeolite peaks were observed in the region 2θ = 18-30°. The comparison of zeolite spectra after acid activation and after metal oxide loading can be observed in Fig. 1.

Based on Fig. 1, it is known that in general the peaks that appear on the diffractogram are not much different from one another. It can be said that the acid treatment, calcination, and impregnation process did not change the zeolite structure. However, there was a change in intensity at several main peaks summarized in Table 1. In addition, new peaks appeared which were characteristic peaks for metal in the region 2θ = 46.199°; 31.290°; 50.947° for Zn, 19.780° and 60.020° for Pb, and 35.646° for Zr. This is supported by the XRD test data carried out for Zn metal showing a characteristic main peak in the area of 45.219° (d = 2.000 Å), 31.113° (d = 2.872Å), and 50.865° (d = 1.793Å). Pb metal showing a characteristic main peak in the area of 19.540° (d = 4.539 Å) dan 61.235° (d = 1.512Å). Meanwhile for Pb did not show significant characteristic peaks with high intensity because of its amount is slightly dispersed in the zeolite. The presence of Pb metal, Zn, and Zr are supported by chemical composition of catalyst in Table 2.

![Fig. 1. XRD diffractogram comparison of ZAA, PbO/ZAA, ZnO/ZAA, ZrO$_2$/ZAA, Pb, and Zn.](image)

<table>
<thead>
<tr>
<th>2θ(°)</th>
<th>ZAA</th>
<th>PbO/ZAA</th>
<th>ZnO/ZAA</th>
<th>ZrO$_2$/ZAA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intensity</td>
<td>D (nm)</td>
<td>Intensity</td>
<td>D (nm)</td>
</tr>
<tr>
<td>22.1007</td>
<td>284</td>
<td>7.154</td>
<td>168</td>
<td>7.297</td>
</tr>
<tr>
<td>25.7400</td>
<td>148</td>
<td>8.480</td>
<td>85</td>
<td>7.950</td>
</tr>
<tr>
<td>26.5200</td>
<td>122</td>
<td>11.911</td>
<td>80</td>
<td>11.760</td>
</tr>
<tr>
<td>27.7228</td>
<td>193</td>
<td>10.278</td>
<td>127</td>
<td>11.554</td>
</tr>
</tbody>
</table>
The intensity of some of the main peaks tended to decrease after acid treatment. Hydrochloric acid causes the release of aluminum species which is outside and within the zeolite framework. Other metals that can dissolve in HCl also come out with aluminum [27]. The same thing happened to zeolites after calcination and oxidation. The peak intensity decreased, presumably because the crystalline water trapped in the framework managed to escape resulting in open zeolite pores. Zeolite carried by metal oxide ZrO$_2$ tends to be more able to maintain the structure of the framework, hence the decrease in peak intensity occurs less. In contrast, ZnO/ZAA catalyst is more brittle and easily damaged in framework structure that the intensity changes are greater. This difference can be observed further based on the nature of the crystals formed. The determination crystal size was obtained from the calculation using the Debye-Scherrer equation from the X-Ray Diffraction data that can be seen in Tables 1.

Based on the data of zeolite crystallinity in Table 2, it is known that ZrO$_2$/ZAA catalyst has the highest crystallinity and has increased after impregnation and oxidation processes. This increase was presumably due to the metal being carried out giving rise to new characteristic peaks with a high intensity that affects the crystallinity of the catalyst. This indicates that the ZrO$_2$ metal oxide is distributed on the zeolite surface. Meanwhile, the decrease in crystallinity in PbO/ZAA and ZnO/ZAA is thought to have occurred due to the metal dispersion process covering the zeolite pores.

Crystal size data show that the ZrO$_2$/ZAA and PbO/ZAA catalysts have a shape that is not much different from the acid-activated zeolite with a range of 6-13 nm. Meanwhile, for ZnO/ZAA catalyst the crystal size increased significantly with a size range of 7-52 nm. This increase in crystal size indicates that the ZnO/ZAA catalyst experiences coagulation or sintering. The crystal grain size can be observed more clearly than the surface morphological image of the zeolite using SEM analysis in Fig. 2.

### Morphological Analysis

Characterization using SEM was carried out to see the surface morphological structure, grain size, structural defects, and contamination composition of a material. The SEM data obtained information on the surface morphology and metal dispersion of the zeolite, while the EDS obtained the chemical composition on the surface of the sample. Fig. 2 shows the surface morphology of the ZAA, PbO/ZAA, ZnO/ZAA and ZrO$_2$/ZAA catalysts with a magnification of 1000 times. In Fig. 2a), the surface micrograph of ZAA shows that the surface structure consists of lamellars with small sizes and there are still lumps. After the metal oxide impregnation process, there was a change in the surface morphology of the zeolite. In PbO/ZAA and ZnO/ZAA catalysts, the grain size of zeolite became larger than that of activated zeolite, especially in ZnO/ZAA the surface morphology was more heterogeneous. This is in accordance with the crystal size calculations in Table 1 which shows the crystal size of ZnO/ZAA is the largest compared to other zeolites. Meanwhile, ZrO$_2$/ZAA in Fig. 2d) shows a smoother and more homogeneous surface structure. This data supports XRD data which shows the metal dispersing process does not occur sintering. The metal oxide is successfully distributed on the zeolite surface.

The chemical composition of zeolites can be determined by EDS analysis which is shown in graphical form in Fig. 2. The percentage composition of

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Catalyst</th>
<th>ZAA</th>
<th>PbO/ZAA</th>
<th>ZnO/ZAA</th>
<th>ZrO$_2$/ZAA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cristallinity (%)</td>
<td></td>
<td>76.739</td>
<td>66.790</td>
<td>41.080</td>
<td>77.117</td>
</tr>
<tr>
<td>Surface area (m$^2$/g)</td>
<td></td>
<td>28.812</td>
<td>18.469</td>
<td>23.317</td>
<td>27.570</td>
</tr>
<tr>
<td>Total pore volume (cc/g)</td>
<td></td>
<td>0.074</td>
<td>0.078</td>
<td>0.093</td>
<td>0.095</td>
</tr>
<tr>
<td>Pore radius (nm)</td>
<td></td>
<td>1.7172</td>
<td>5.3021</td>
<td>1.5685</td>
<td>1.6750</td>
</tr>
<tr>
<td>Composition (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td></td>
<td>51.34</td>
<td>71.39</td>
<td>72.12</td>
<td>62.34</td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td>28.89</td>
<td>22.72</td>
<td>20.87</td>
<td>29.64</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>2.03</td>
<td>3.65</td>
<td>4.02</td>
<td>3.55</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>-</td>
<td>0.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td>-</td>
<td>-</td>
<td>0.18</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.63</td>
</tr>
<tr>
<td>Impurities</td>
<td></td>
<td>1.74</td>
<td>2.11</td>
<td>2.83</td>
<td>2.92</td>
</tr>
</tbody>
</table>
the zeolite components is summarized in Table 2. Based on the EDS data, it can be seen that the percentage of metal that has been successfully carried from the 1% metal impregnation treatment. Only 0.12% and 0.18% carry Pb and Zn respectively, while Zr is carried more than 1%. In addition, other impurity elements have decreased after impregnation and oxidation processes so that the modified zeolite becomes cleaner. In this case the calcination and oxidation processes play an important role in removing alkaline metal impurities such as K, Ca, Mg, Na, and evaporating crystalline water and CO₂ from the zeolite framework so as to increase the catalytic activity of the catalyst. The calcination process with high temperature as a thermal activation changes metal hydroxides into active metal oxides on the catalyst [28].
N₂ Gas Sorption Analysis

BET analysis provides a graph form of the adsorption-desorption isotherm of N₂ gas at ZAA, PbO/ZAA, ZnO/ZAA, ZrO₂/ZAA as shown in Fig. 3. The graph shows the existence of loop hysteresis at a relative pressure of 0.4-0.9 so it is classified as a type IV in accordance with the IUPAC classification. The existence of loop hysteresis and high graph increase in P/P₀ characterize that ZAA, PbO/ZAA, ZnO/ZAA, ZrO₂/ZAA have mesoporous and micropores in their structure [29].

Based on the data in Table 2, it is known that the specific surface area of the catalyst generally decreases after the impregnation process of Pb, Zn, and Zr metals. The total pore volume is in the range of 0.07-0.09 cc/g. Meanwhile, the mean pore radius of the ZAA, ZnO/ZAA, PbO/ZAA, and ZrO₂/ZAA show that the catalysts are mesoporous material (pore diameter 2-50nm). The total pore volume increases after metal loaded. Song et al. (2013) [30] reported that metal support layer can increase the pore volume of the molecular sieve that can improve the selectivity of catalysts. Metal loading is indicated to block some micropores, causing a decrease in the surface area [31]. The highest reduction in surface area occurred in PbO/ZAA catalysts up to 35.89%, but at the same time new mesopores were formed on the PbO/ZAA catalyst due to the superposition of the metal layer on the zeolite surface.

Catalyst Activity Test in Biodiesel Synthesis

Rubber seed oil that has been obtained from the extraction process with n-hexane solvent is then synthesized into biodiesel with an oil: methanol ratio of 1:6, 5% catalyst (w/w oil), and the process conditions at 60°C for 1 hour. The test results for the characteristics of rubber seed oil and biodiesel are summarized in Table 3.

The comparison of the amount of biodiesel yield conversion can be observed in Fig. 4. Biodiesel synthesized using ZrO₂/ZAA catalysts has the highest yield with the highest percentage reaching 58.10%. The water content of the extracted rubber seed oil was high enough to reach 2.67% and after the synthesis process decreased the water content to 0.092% but did not meet ASTM standards. While the density and FFA content of biodiesel have met the standards, the biodiesel density of each catalyst is in the range of 0.8 g/cm³ and the FFA content is below 2%. The graph of the comparison of FFA levels before and after the reaction can be seen in Fig. 4. The low FFA levels in the synthesized biodiesel indicate an esterification reaction has been occurred and free fatty acids are successfully converted into methyl esters.

To determine the fatty acid composition of the oil and the methyl ester composition formed during the synthesis process, GC-MS analysis was performed. The content of fatty acids and methyl esters in RSO and biodiesel are summarized in Table 4.

Based on the GC-MS analysis data in Table 4, it is known that some of the main fatty acids contained in rubber seed oil are linoleic acid, linolenic acid, palmitic acid, and stearic acid. These fatty acids are then converted into their fatty acid methyl ester (FAME) form during the esterification and transesterification processes. The ZrO₂/ZAA catalyst showed the best performance in converting the total FFA to FAME up to 86.52%, while the PbO/ZAA and ZnO/ZAA catalysts reached 39.99% and 33.58%, respectively. It can be seen that in PbO/ZAA and ZnO/ZAA there is a number of palmitic acid which is not converted while...
in ZrO₂/ZAA there is a number of unconverted stearic acid.

There is a significant difference between the conversion results using an acid activation catalyst and a metal oxide embedded catalyst. The difference in the number of conversions with various catalysts is closely related to the ability of the catalyst to convert these compounds seen from the zeolite character and the presence of metal oxides as basic site in zeolite. Metal-bearing zeolites produce a bifunctional catalyst having both of acidic and basic site. So that the metal loaded on zeolite can increase the ability to convert oil into biodiesel. In addition, calcination was also found to be an important factor for the high strength of active site and surface area due to the formation of the active crystal structure [32].

Fig. 4. Graph of yield and FFA reduction in biodiesel.

![Graph of yield and FFA reduction in biodiesel.]

Fig. 5. The reaction mechanism of biodiesel production using both of acidic and basic site catalysts.

![Reaction mechanism of biodiesel production using both of acidic and basic site catalysts.]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>% Area</th>
<th>RSO</th>
<th>PbO/ZAA</th>
<th>ZnO/ZAA</th>
<th>ZrO₂/ZAA</th>
</tr>
</thead>
<tbody>
<tr>
<td>9,12-Octodecadienoic acid (linoleic acid)</td>
<td>C₁₉H₃₄O₂</td>
<td>32.86</td>
<td>-</td>
<td>19.86</td>
<td>18.44</td>
<td>32.86</td>
</tr>
<tr>
<td>9,12,15-Octodecatrienoic acid (Linolenic acid)</td>
<td>C₁₉H₃₂O₂</td>
<td>12.01</td>
<td>-</td>
<td>0.32</td>
<td>0.42</td>
<td>12.01</td>
</tr>
<tr>
<td>Hexadecanoic acid (Palmitic acid)</td>
<td>C₁₉H₃₂O₂</td>
<td>0.33</td>
<td>14.49</td>
<td>0.30</td>
<td>14.08</td>
<td>8.01</td>
</tr>
<tr>
<td>Octadecanoic acid (Stearic acid)</td>
<td>C₁₉H₃₄O₂</td>
<td>24.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9,12-Octodecadienoic acid, methyl ester (Methyl linoleate)</td>
<td>C₁₉H₃₄O₂</td>
<td>5.51</td>
<td>-</td>
<td>-</td>
<td>12.01</td>
<td>14.08</td>
</tr>
</tbody>
</table>
The possible reaction mechanisms between reactants and bifunctional catalysts based on acidic and basic sites are shown in Fig. 5. Molecular reactants diffuse inside the zeolite pore. Zeolites are embodied metal oxides with Bronsted and Lewis acid sites of active zeolites and basic sites of metal oxides. FFA is adsorbed on the acid site while methanol is adsorbed on the basic site. Protons on the zeolite acid site bind to oxygen in FFA, while metal oxides bind to protons in methanol. The intermediate products are formed by nucleophilic attack of the alcohol into esters at both acidic and basic sites [33, 34]. The hydroxyl is then released in the form of water molecules from the esterification reaction at the acid site while glycerol is formed as by product of the transesterification reaction at basic site [35]. Furthermore, the water and glycerol formed are desorbed from the surface of the catalyst as the final product.

ZrO2/ZAA catalyst gives the best performance in synthesizing biodiesel compared to ZAA, PbO/ZAA, and ZnO/ZAA. This is supported by the character of the synthesizing biodiesel compared to ZAA, PbO/ZAA, and environmentally friendly alternative fuels with great potential for RSO to be developed as a renewable and biodiesel density. As a whole, these data show a significant improvement in the production of biodiesel from rubber seed oil.

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**Conclusions**

The conversion of rubber seed oil to biodiesel has been carried out using bifunctional catalysts PbO/ZAA, ZnO/ZAA, and ZrO2/ZAA through a one-stage esterification/transesterification reaction. The best catalyst performance is shown by ZrO2/ZAA which is capable of measuring up to 58.10%. The high FFA content in RSO was successfully converted to MEFA until the levels were reduced by 86.22%. These abilities are closely related to the character of ZrO2/ZAA which is better than PbO/ZAA and ZnO/ZAA catalysts, including high crystallinity reaching 77.12%, uniform surface morphology and small crystall grains. Moreover, this catalyst has a large specific surface area and a high total pore volume. These results indicate that the activation and modification processes with the addition of metal oxides can increase the character and catalytic activity of the catalyst. In addition, the biodiesel products produced in this study have met ASTM standards for FFA content and biodiesel density. As a whole, these data show a great potential for RSO to be developed as a renewable and environmentally friendly alternative fuels with heterogeneous based catalyst. Therefore, continuous efforts to modify both heterogeneous catalysts and production methods need to be carried out intensively in the future to increase the effectiveness of biodiesel production from rubber seed oil.

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**Conflict of Interest**

The authors declare no conflict of interest.

**References**

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