Preparation of activated carbon-based catalyst from nipa palm (Nypa fruticans) shell modified with KOH for biodiesel synthesis

Taslim\textsuperscript{1,2}, Iriany\textsuperscript{1,2}, O Bani\textsuperscript{*}, E Audina\textsuperscript{1} and R Hidayat\textsuperscript{1}

\textsuperscript{1}Department of Chemical Engineering, Faculty of Engineering, Universitas Sumatera Utara, Medan, North Sumatra 20155, Indonesia
\textsuperscript{2}Center of Excellence for Natural Resources Based Technology, Universitas Sumatera Utara, Medan, North Sumatra 20155, Indonesia

\textsuperscript{*}Email: oktabani@usu.ac.id

Abstract. An attempt to synthesize a low-cost carbon-based heterogeneous catalyst from biomass has been explored. The focus of this research was investigating the carbon-based catalyst from nipa palm shell modified with KOH in biodiesel synthesis. Dry nipa palm shell powder was carbonized at 300°C for 1 h to produce carbon. The carbon was then modified by impregnation with potassium hydroxide (KOH) solution. The carbon and modified carbon were analyzed by SEM-EDX. The modified carbon was applied as a heterogeneous catalyst in transesterification of palm oil and methanol. Transesterification was carried out at 60°C and stirred at 300 rpm. Reaction time and catalyst load was observed. Highest biodiesel yield of 95.5% was obtained at 2 h reaction time, 3% catalyst load, and methanol to oil ratio of 12:1. This preliminary study confirmed that KOH-modified carbon may act as a heterogeneous catalyst in biodiesel synthesis.

1. Introduction
The increasing demand for energy has prompted various parties to look for alternative fuels. One alternative fuel is biodiesel which can be produced from vegetable oil or animal fat through alcoholysis (transesterification) process with the aid of a catalyst. A variety of catalysts can be used such as homogeneous catalysts or heterogeneous catalysts. Heterogeneous catalysts have many advantages over homogeneous catalysts including less liquid waste, easier separation of catalyst, reusability, and can be synthesized from biomass waste [1-4].

Biomass has been used as a precursor heterogeneous catalysts synthesis. The main content of biomass is generally cellulose, hemicellulose, lignin, and a small amount of extractive substances and minerals. For biomass containing high minerals, after the calcination process the resulting ash can be used directly as a catalyst [1,5]. As for biomass with low mineral content, the biomass is first converted to carbon and then the desired active component is attached. Synthesis of catalysts from biomass can reduce the cost of catalyst production, as well as alleviate agricultural waste problem. Every year, the agricultural sector produces more than 5 billion metric tons of biomass waste [5]. One of the agricultural wastes is nipa palm shell which is the outermost part of the nipa fruit after the pulp is taken. Nipa palm fruit flesh is often used as juice or other food products while the fibrous shell has the potential to be used as a carbon source.
Activated carbon from biomass has large pores and surface area, so that by slight modification, it can be used as catalyst precursor in biodiesel synthesis [6]. Because activated carbon has many mesopores, bases such as KOH or NaOH are readily adsorbed on the surface during chemical treatment. Modification by impregnation with KOH solution may increase catalytic activity of the activated carbon significantly [7]. Aside of being cheap and sustainable, carbon-based catalysts have other advantages such as acid and alkaline resistance, modifiable hydrophobicity/hydrophilicity properties, higher structural stability at high temperature, and amphoterism due to presence of oxygenated functional groups. These advantages allow carbon for better metal absorption and catalyst dispersion. Carbon shape is also modifiable into granules, pellets, fibers and others [8,9].

The use of activated carbon as catalyst support has been reported in several literatures such as activated carbon derived from candlenut shell [10], palm shell [11], flamboyant pods [12] and shea nut shell [13]. However, utilization of activated carbon from nipa palm fiber has not been reported. Therefore, the focus of this research was investigating nipa palm shell as a carbon precursor for catalyst support modified through impregnation with KOH solution, and its application in biodiesel synthesis.

2. Materials and Methods

2.1. Materials
Nipa palm shell were obtained from farmers in Talawi District, Batu Bara Regency, North Sumatra. Chemicals such as hydrochloric acid, methanol, ethanol and potassium hydroxide were purchased from local suppliers. Refined bleached and deodorized palm oil (RBDPO) was supplied by PT Multimas, Indonesia. The free fatty acid, moisture, density and kinematic viscosity of the RBDPO were 0.02%, 0.1%, 916 kg/m$^3$, 24 mm$^2$/s respectively.

2.2. Preparation of catalyst
Nipa palm shell was washed with running water to remove dissolved impurities and dried for 2-3 days under the sun. Further drying was carried out in an oven at 105°C till constant weight. Dried nipa palm shell was crushed using a commercial blender until powdered. Nipa palm fruit, the cross section and nipa palm flesh is in Figure 1, while dried nipa palm shell and the powder are in Figure 2.

![Figure 1](image_url)
The powder was carbonized in a furnace at 300°C for 1 h. The carbon was cooled to room temperature then washed with 0.1 M HCl at carbon to HCl ratio of 1:6 (w/v) to remove impurities. Afterwards, it was neutralized with deionized water to pH of 7. Activated carbon was dried again in an oven for about 2 h at 105°C. A much as 10 g activated carbon was impregnated with KOH solution at a concentration of 50 g/150 ml deionized water. The impregnation was carried out at room temperature for 24 h under constant stirring. Activated carbon was separated from the mixture by filtration and dried in an oven at 200°C for 0.5 h, followed by calcination at 500°C for 3 h. This modified carbon was ready to be used as a catalyst, stored in a closed container, and characterized using SEM-EDX and FTIR.

2.3. Transesterification

As much as 50 g coconut oil was placed into a three-necked flask equipped with a heater, stirrer, condenser, and thermometer. Meanwhile, methanol (methanol to oil ratio of 12:1) and catalyst (2-5% load) was stirred for 60 min in a closed glass beaker and placed into a three-necked flask. The reaction was carried out at 60°C and stirring speed of 300 rpm. Reaction time was varied from 90-150 min. Product was separated from the catalyst by filtration. Purification of biodiesel was carried out by washing with warm water followed by drying at 105°C. The product was analyzed for its physical properties and compared with European standards.

3. Results and Discussion

3.1. SEM-EDX analysis

The morphology of nipa fruit shell powder and the carbon carbonized at 300°C for 1 h were analyzed using SEM. The SEM results are in Figure 3. In Figure 3(a), nipa palm shell powder surface was shiny, irregular, has larger inter-particle cavity, agglomerated with non-uniform particle size and pore. In Figure 3(b), carbon surface had cracks and fissures, but still agglomerated, had smaller particle size and pores of different shapes and sizes. In addition, the number of pores increased so that surface area increased. However, it still contained a number of impurities. The formation of pores is very important because it provides sites for KOH attachment during impregnation. The surface of modified carbon after KOH impregnation and calcination was covered with potassium as in Figure 3(c). This phenomenon confirms that KOH had penetrated into the pores and was dispersed on pore surface. Similar findings was also reported by other researchers [6,10-12].
Figure 3. SEM analysis of (a) nipa palm shell powder, (b) carbon from nipa palm shell, c) modified carbon

EDX results of nipa palm shell powder, carbon from nipa palm shell and modified carbon are in Table 1. Nipa palm shell was composed mainly of C and O. During carbonation, volatile substances was thermally decomposed, forming pores and increasing the surface area. Carbon content also increases during carbonization, while oxygen content decreases. In addition, carbon will fuse to form more stable bonds, while other compounds are broken down or evaporated [14]. After KOH impregnation and calcination, carbon decreases and oxygen increased. The decrease in carbon content is due to carbon reaction with KOH to form metal oxides K2O and K2CO3 following these reaction equations [15]:

\[
\begin{align*}
C + 4 \text{KOH} & \rightarrow \text{K}_2\text{O} + \text{K}_2\text{CO}_3 + 2 \text{H}_2 \\
C + \text{K}_2\text{O} & \rightarrow 2\text{K} + \text{CO} \\
C + \text{K}_2\text{CO}_3 & \rightarrow 2\text{K} + 3\text{CO}
\end{align*}
\]

The active compounds, K2O and K2CO3, have important roles in catalyzing transesterification [10, 17].

Table 1. Elemental composition of nipa palm shell powder, carbon from nipa palm shell and modified carbon

| Element | Nipa palm shell | Carbon | Modified carbon (after KOH impregnation and calcination) |
|---------|----------------|--------|---------------------------------------------------------|
| C       | 56.83          | 71.65  | 52.57                                                   |
| O       | 38.65          | 12.11  | 27.52                                                   |
| Na      | 0.88           | 1.26   | -                                                       |
| Mg      | 0.21           | 0.28   | 0.40                                                    |
| Al      | -              | 0.07   | -                                                       |
| Si      | -              | 0.30   | 0.46                                                    |
| P       | 0.10           | 0.16   | 0.12                                                    |
| S       | 0.10           | 0.24   | -                                                       |
| Cl      | 1.58           | 11.86  | -                                                       |
| K       | 1.65           | 2.06   | 18.93                                                   |

3.2. Transesterification
To observe the effect of catalyst load on biodiesel yield, experiments were carried out by varying catalyst load from 1 to 4% at reaction temperature of 60°C, methanol to oil molar ratio of 12:1, and
reaction time of 2 h. In Figure 4, yield increased with catalyst load up to 3%, then decreased afterwards. Further addition of catalyst may increase the viscosity of reaction mixture, renders reactant molecules less effective mixing, and require more rigorous mixing [16]. In addition, separation of catalyst from product mixture becomes harder. In such conditions, leaching may occur in which metal oxides in the catalyst react with triglycerides to form soaps [12]. Determination of the right amount of catalyst depends on the type and source of the catalyst used. The optimum amount in this study was 3% which yielded 95.5% biodiesel. The yield achieved in this study was slightly lower than previous study using candlenut shell as carbon precursor [10], but higher than that using flamboyant pods as carbon precursor [12], in which the yields reached 96.65 and 89.81%, respectively.

Figure 4. Effect of catalyst load on biodiesel yield

Figure 5. Effect of reaction time on biodiesel yield

Transesterification was also affected by reaction time as in Figure 5. Reaction time was varied from 90 to 180 min for reaction temperature of 60°C, 3% catalyst load, and methanol to oil molar ratio of 12:1. Biodiesel yield increased with reaction time up to 120 min. A longer time resulted in good
contact between the reactants, thus yield increased. However, excessive reaction time will decrease yield. Transesterification reaction is reversible. Once equilibrium is achieved, further addition of reaction time will reverse reaction to form fatty acids and suppress biodiesel formation. In addition, longer reaction time may result in overheating of reaction mixture, loss of solvent, and energy loss [18]. The best reaction time in this study was 2 h, with yield reaching 95.5%. The optimum reaction time of 3 h has also been reported in several previous studies [10,19].

3.3. Biodiesel Properties

Analysis of physical properties was carried out to qualify the biodiesel. Some of the observed physical properties are in Table 2, then compared with the European standard (EU 14214). The results confirmed that biodiesel produced in this study had met the existing standards. It also indicated that carbon modified with KOH can be applied as a catalyst in biodiesel synthesis.

| Physical properties       | Unit   | Biodiesel produced | EN 14214 |
|--------------------------|--------|--------------------|----------|
| Methyl ester content     | %      | 98.1               | >96.5    |
| Density                  | kg/m³  | 875                | 860-900  |
| Kinematic viscosity      | mm²/s  | 4.5                | 3.5-5.0  |

4. Conclusion

Nipa palm shell can be used as a sustainable carbon precursor through carbonization. Carbon modification by KOH impregnation followed by calcination resulted in a heterogeneous catalyst. This catalyst contains K₂O and K₂CO₃ which contribute in catalyzing the transesterification. The highest yield in this preliminary study reached 95.5% at 3% catalyst load, 60°C reaction temperature, 2 h reaction time, and methanol to oil molar ratio of 12:1.

References

[1] Taslim, Irawan F and Iriany 2020 IOP Conf. Ser.: Mater. Sci. Eng. 1003 01212
[2] Zabeti M, Daud W M A W and Aroua M K 2009 Fuel Process. Technol. 90 770
[3] Refaat A A 2011 Int. J. Environ Sci Technol. 8 203
[4] Taslim, Iriany, Tambak M N and Bani O 2020 Int. J. Eng. Res. Tech. 13 3298
[5] Balaji M and Niju S 2020 Renew. Energy 146 2255
[6] Abu-Jrai A M, Jamil F, Al-Muhtaseb A H, Baawain M, Al-Haj L, Al-Hinai M, Al-Albri M and Rafiq S 2017 Energy Convers. Manage. 135 236
[7] Wang S, Yuan H, Wang Y and Shan R 2017 Energy Convers. Manage. 150 214
[8] Rodriguez R F 1998 Carbon 36 159
[9] Lam E and John Luong H T 2014 Catalysis 4 3393
[10] Taslim, Bani O, Iriany, Aryani N and Kaban G S 2018 Key Eng. Mater. 777 262
[11] Baroutian S, Aroua M K, Abdul Raman A A and Nik Sulaiman N M 2010 Fuel Process. Technol. 91 1378
[12] Dhawane S H, Kumar T and Halder G 2016 Renew. Energy 89 506
[13] Dejean A, Ouedraogo I W K, Mouras S, Valette J and Blin J, 2017 Energy Sustain. Dev. 40 103
[14] Kwiatkowski M, Kalderis D and Diamadopoulos E 2017 J. Phys. Chem. Solids 105 81
[15] Yang L, Xue-Wei C, Li C, Xiang-Li L and Yuan W K 2013 J. Indus. Eng. Chem. 19 784
[16] Taslim, Sinaga B A, Sihaloho M N, Iriany and Bani O 2019 J. Phys.: Conf. Ser. 1175 012281
[17] Gohain M, Devi A and Deka D 2017 Industrial Crop & Products 109 8
[18] Patil P D, Gude V G, Mannarswamy A, Deng S, Cooke P, Munson-McGee S, Rhodes I, Lammers P and Khandan N N 2011 Bioresour. Technol. 102 118
[19] Aleman-Ramirez J L, Moreira J, Torres-Arellano S, Longoria A, Okoye P U and Sebastian P J 2021 Fuel 284 118983