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Manufacturing the activated carbon catalyst of impregnated palm core shells for biodiesel production

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ABSTRACT

This research aims to produce activated carbon-based heterogeneous catalyst derived from palm kernel shells impregnated with a KOH solution and to determine the effects of the concentration of the KOH solution and the time period during impregnation. The variables observed included KOH concentration and impregnation time. The impregnation process used KOH solution with the solution concentrations of 1N, 2N, 3N, 4N and 5N with impregnation process within 18 hours, 21 hours and 24 hours. AAS, FTIR and SEM were analyzed after impregnation with different concentrations and times. The results of the analysis of potassium metal showed the highest absorption occurred at a concentration of 5N within 21 hours at 25.4570%. The application of the activated carbon catalyst from palm kernel shells was conducted in making biodiesel. The process of making biodiesel was carried out with a reaction time of 120 minutes at a temperature of 60°C with a molar ratio of 1: 12 using a catalyst of 2% (% w/w). Biodiesel yield testing referred to SNI 04-7182-2015. The analysis results obtained showed 879 kg/m3 density, 6.1 cst viscosity, 0.5 acid number, and 174°C flash point.

1. Introduction

Palm kernel shells, along with the increasingly rapid era development, become one of the wastes commonly produced in the palm oil processing. As revealed by the Indonesian Ministry of Agriculture, the amount of palm kernel shell waste reaches 60% of the kernel oil industry. They have a shape similar to coconut shells, but harder and thicker. Most of the palm oil productions produce waste in the form of shells. As a by-product of the palm oil industry, palm kernel shells in fact have several different potential uses.

Activated carbon can be produced from various natural materials, including palm oil shells, egg shells, banana peels, empty fruit bunches, and other natural materials that possess a high carbon content that can be used to make carbon [1]. The activated carbon is highly good to be used as an adsorbent in the adsorption process for having better adsorptive capacity.

Carbon materials are also frequently used as they can be a good support, have an inert surface that can be modified and have large pores. Also, they are often used as catalyst supports. Activated carbon contains a number of functional groups, such as various chemical groups attached to the active carbon structure, in addition to carbon atoms. Chemically reactive carbon surfaces, for example, are functional groups that can change the adsorption characteristics of the material [2]. The impregnation method can be used to make catalysts containing activated carbon. This technique is quite simple to be done as it involves contacting porous support particles with a solution that functions as an active site.

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In common, impregnation is interpreted as a process of completely saturating certain substances into a material or substrate. By immersing the support in a solution containing active metal, in this case KOH solution, which functions as an active site in the impregnation process, then the support pores will be filled with the active metal solution through the metal adsorption process. Active sites refer to the places where chemical reactions occur in. When the catalyst is supported on the surface of activated carbon, the active sites are evenly distributed over a wide surface in that the activated carbon has a high surface area due to its complex pore structure. Thus, the chemical reaction occurred at an active site can efficiently take place as the contact surface between the catalyst and the reactant material becomes wider and the use of support aims to obtain the optimum distribution of the catalyst material to make the reaction surface area larger [3].

This experiment was also assisted by supporting tools, such as AAS, FTIR and SEM. AAS (atomic absorption spectroscopy) analysis purposely to determine how much potassium concentration was absorbed into the activated carbon after impregnation. To determine the functional groups present in the activated carbon before and after impregnation, FTIR (Fourier Transform Infra Red) analysis was conducted. Meanwhile, SEM (Scanning electron microscopy) analysis aimed to determine the pores contained in the activated carbon.

The activated carbon of palm kernel shells with a KOH imgranan solution became a catalyst after going through the impregnation process. A catalyst refers to a substance that can reduce the activation energy as well as increase the rate of a chemical reaction, but it does not change permanently in the reaction. To test the catalyst, application of making biodiesel was conducted. In the reaction of biodiesel production, the activated carbon, which has a large surface area, can be used as a catalyst support [4].

Biodiesel is an environmentally friendly renewable energy that has its better emissions produced. Compared to diesel from petroleum, it also has a lower sulfur content. In making biodiesel, transesterification was carried out with a reaction time of 120 minutes at a temperature of 60°C with a molar ratio of 1: 12 with a catalyst of 2% w/w. In this case, biodiesel yield testing refers to SNI 04-7182-2015.

This research aims to determine whether active carbon from palm kernel shells is good for use in making catalysts and to figure out variations in concentration and time during the impregnation process.

2. Materials and Methods

In this research panel, the manufacture of activated carbon from palm kernel shells was carried out with a four-hour carbonation in a muffle furnace at a temperature of 500°C. After grinding, the carbon was crushed using an 80 mesh sieve. The sieved activated carbon was then activated using an HCl solution prior to be impregnated using KOH. The sieved activated carbon was activated with 0.1 M HCl solution to remove any impurities.

The activated carbon was impregnated with KOH with various impregnation times, i.e. 18, 21 and 24 hours with KOH concentrations of 1 N, 2 N, 3 N, 4 N and 5 N and at impregnation temperature at 30°C. Subsequently, an analysis was conducted by means of AAS, FTIR and SEM tools.

The process of making biodiesel was carried out for 120 minutes at a temperature of 60°C with a molar ratio of used cooking oil: methanol of 12:1 on a catalyst impregnated with KOH using 2% w/w of used cooking oil. Following this, the mixture was centrifuged to form two phases in which the upper phase was methanol, biodiesel and glycerol; while the lower phase was the catalyst. The separation of the mixture was done by decanting using a separating funnel for 12 hours. Meanwhile, washing the methyl ester was done using distilled water to remove any glycerol and remaining impurities. It was continued with the analysis of acid number, kinematic viscosity at 40°C, density at 40°C, water content and flash point of biodiesel.

Palm kernel shells were then dried at 150°C for 3 hours in which the result of the drying was carbonated at 500°C for 4 hours. The carbonation subsequently was refined and sifted to obtain finer particles. Before going to be impregnated with KOH solution to activate the catalyst, the particles were firstly washed to remove any remaining dirts. The impregnation was then dried in an oven to remove any remaining water. This was repeated to ascertain that the particles were completely dry. The particles were then analyzed to determine the quality of the catalyst in which the analysis showed that the catalyst was a KOH activated carbon catalyst. Afterwards, the catalyst was refluxed to remove any remaining impurities and separated in stage 1 to separate the biodiesel from glycerin and other impurities. This resulting biodiesel was purified to remove any remaining impurities. The biodiesel later on went to separation stage 2 to separate the purer biodiesel in which the resulting biodiesel was heated to remove any remaining water. The resulting biodiesel was then subjected to Biodiesel Test Analysis to determine its quality, including Viscosity, Acid Number, Density and Flash Point.

3. Results and Discussion

In this research, catalyst was made from palm kernel shells impregnated with KOH and tested in the biodiesel production process. In making catalysts, activated carbon from palm kernel shells comprised a number of stages: drying, carbonation, activation and impregnation. Drying stage aimed to remove the water content and reduce the volatile substances contained in the palm kernel shell. Further, in the carbonation process, the palm kernel shells were placed in a furnace at a temperature of 500°C within 4 hours. Having conducted carbonization, it went to activation process. Activation is a part of the active carbon manufacturing process purposely to open or create pores through which adsorbents can pass or to increase the distribution capacity, pore size and surface area of activated carbon with physical or chemical treatment [5].

Having conducted carbonation and activation process, the activated carbon was again dried using an oven to remove the water content after activation and continued with impregnation using a KOH solution. The activated carbon with KOH activator is able to absorb compounds better [6]. The impregnation process aimed to fill empty pores by absorbing potassium ions contained in the KOH solution through ion adsorption. During impregnation, K+ ions were absorbed into the empty pores, while OH- ions was bound to H2O. This carbon containing KOH is a catalyst in the biodiesel making process. The process of making biodiesel involves stirring and heating to activate the KOH ions contained in the catalyst to speed up the reaction to produce biodiesel.

3.1. Analysis of active carbon characteristics from palm kernel shells

The properties of activated carbon were tested with volatile matter content, water level and ash. In the study of active carbon from palm kernel shells, it was especially done with volatile analysis. The flying substance obtained was 0.4%. The increasing carbonization temperature tended to reduce the volatile matter content. This occurs as the decomposition of non-carbon compounds takes place completely at high temperatures [7]. A higher carbonization temperature will increase the amount of water that evaporates from the carbonization material, making the water content in the coal getting lower. Thus, it can be concluded that the water content in the analyzed palm shell activated carbon was 0.54μn similar with the water content parameters based on the standard of SNI 06-3730-1996, which is mostly 15%. Testing the ash content showed that the level was 6.67% suitable with SNI 06-3730-1995 with the maximum of 10%.

3.2. Analysis of the effects of KOH concentration on potassium absorption in activated carbon from palm kernel shells impregnated with KOH

The impregnation process involved 5 different concentrations to identify the effects of the absorbed KOH concentration on the activated carbon. To determine the percentage of potassium content absorbed by activated carbon, analysis was carried out using AAS (atomic absorption spectroscopy). Figure 1 shows the results of AAS analysis showing the effects of absorption concentration on activated carbon.

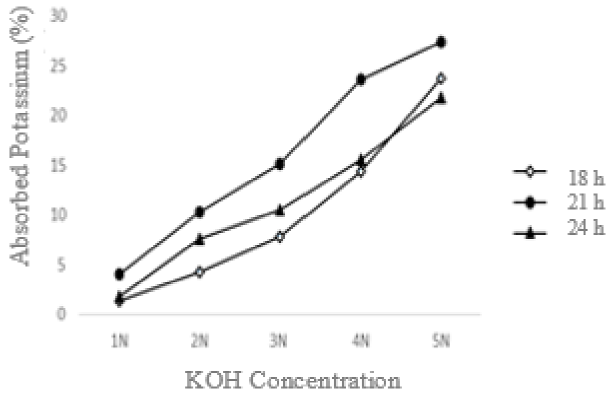

Fig. 1. Graph of the relationship between potassium metal absorption and KOH concentration over time

The figure shows that the highest metal potassium content occurred at a concentration of 5 N. The ratio or concentration of KOH used in activated carbon impregnation affects the content and catalytic properties of activated carbon after impregnation. The increase of the concentration of the KOH solution will increase the active catalyst content in the catalyst support (active carbon). In this study, the best absorbed concentration of potassium metal was 5 N in comparison to other concentrations. The best metal absorption was at a KOH concentration of 5 N with a time of 21 hours with potassium metal absorption of 25.4570% compared to other concentrations. This indicated that the absorption of potassium metal from activated carbon from palm shells produced a higher potassium content after being impregnated with a KOH solution.

3.3. *Analysis of the effects of KOH time on potassium absorption in activated carbon from palm kernel shells with KOH impregnated*

Soaking was done within 18 hours, 21 hours and 24 hours. Figure 1 shows the effects of time and concentration on the absorption of adsorbed potassium metal in which it was found that the concentration of 5 N always increased with time.

A prolonged time will allow activated carbon to absorb the highest amount of KOH solution, but when it reaches saturation and equilibrium, a longer soaking time will not affect the absorption as much as potassium metal [8]. In this study, the best results were obtained for the absorption of potassium metal, namely at a concentration of 5 N with a time of 21 hours, namely 25.457.

3.4. *FTIR (fourier transform infra red) analysis*

FTIR (Fourier Transform Infrared) analysis aims to determine new groups in the activated carbon of palm kernel shells after impregnation with KOH. Figure 2 and Figure 3 depict the results of FTIR (Fourier Transform Infrared) analysis of activated carbon of palm kernel shells before impregnation and after impregnation with KOH.

As seen from Figure 2 and Figure 3, there were differences in waves. At the waves of 3200-3550 cm-1, the carboxyl monomer group –OH was formed, similar with the results of research conducted by Tan et al. 2019. At waves around 1400 cm-1, this indicated carbonate compounds.

The carbonate compound formed after impregnation was K2CO3, where potassium was bound to carbonate compound. Potassium carbonate is the active ingredient responsible for catalyzing transesterification. When activated carbon is modified with KOH, acid neutralization can occur on the carbon surface [9].

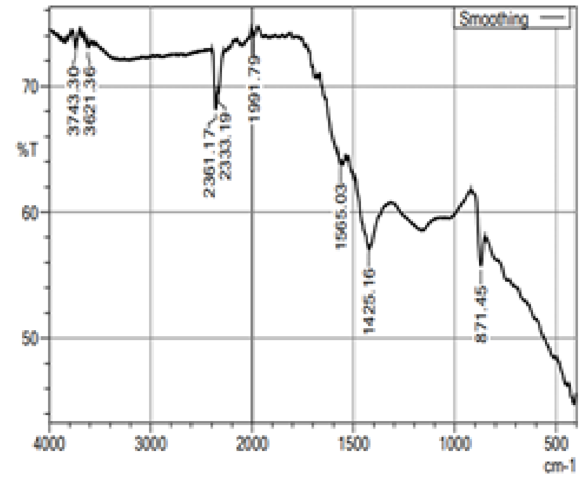

Fig. 2. FTIR (fourier transform infrared) analysis before KOH impregnation

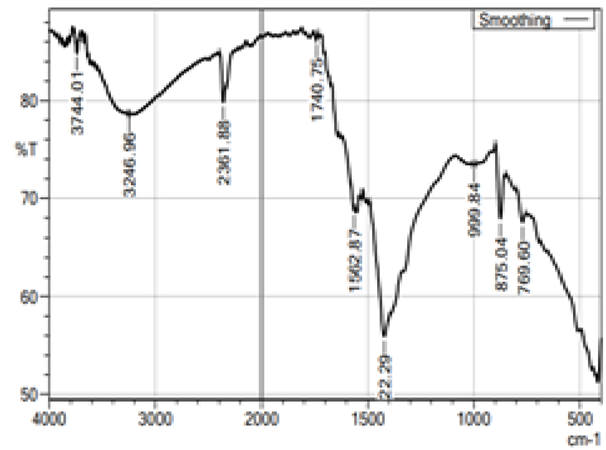

Fig. 3. FTIR (fourier transform infrared) analysis after KOH impregnation

During the impregnation process, KOH compounds can react with carbon. The reactions occurred are presented as follows.

$$4\,KOH + C \longrightarrow K_2CO_3 + K_2O + 2H_2$$
$$K_2O + C \longrightarrow 2K + CO$$
$$K_2CO_3 + C \longrightarrow 2K + 3\,CO$$

Having conducted FTIR (Fourier Transform Infrared) analysis, group changes occurred in the activated carbon after and before impregnation.

3.5. *SEM (scanning electron microscopy) analysis*

SEM (Scanning Electron Microscopy) analysis aims to determine the morphology in the activated carbon. In the impregnation process, activated carbon that had already had a pore structure on its surface was soaked in a KOH (Potassium Hydroxide) solution. During impregnation, KOH absorbed into the pores of the activated carbon and interacted with the surface of the activated carbon. Figure 4 and Figure 5 depict the results of SEM analysis.

Figure 4 depicts the results of the activated carbon analysis before impregnation. There were a number of pores that were still large and fibrous, indicating the surface area available for activation and catalysis [10]. Therefore, the absorption process will increase. This, later on, causes an increase in the absorption capacity of potassium ions in activated carbon. The pores of activated carbon are still large as the activation process will dissolve impurities so that the pores are more open. It can be concluded that the organic material burnt or oxidized during the calcination and carbonation processes will produce a hollow matrix on the catalyst surface [11].

There was a difference between the results of SEM analysis before and after impregnation. Figure 5 shows the results of SEM analysis after impregnation.

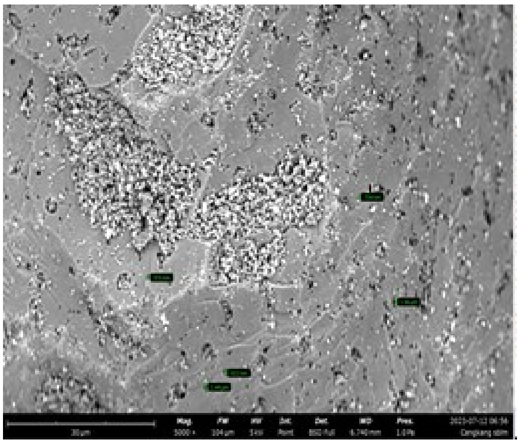

Fig. 4. SEM (scanning electron microscopy) analysis before KOH impregnation

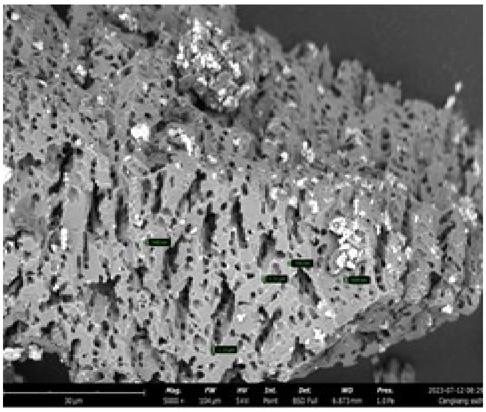

Fig. 5. SEM *(scanning electron microscopy)* analysis after KOH impregnation

3.6. Analysis of catalyst application in biodiesel production

The application of making biodiesel aimed to determine the performance of the palm kernel shell catalyst which has been made with KOH impregnation. The process of making biodiesel went through the transesterification stage. To balance the transesterification reaction, a catalyst was used. Alkaline catalysts are those which are highly important in industry. It can be used to obtain corn oil methyl esters and can be homogeneous or heterogeneous [12]. Research using activated carbon catalysts from palm kernel shells impregnated with KOH (Potassium Hydroxide) is interesting to research. In this context, palm kernel shells are used as a support or carrier for KOH, which acts as an activation agent to form an active carbon catalyst.

Biodiesel production was carried out with 2% catalyst at a temperature of 60°C within 2 hours, which resulted in a yield of 90.35%. In research conducted by Susanti et al. [13], the yield obtained was 85% with 1% catalyst at a temperature of 65°C and research conducted by Tang et al. used 1.5% catalyst with a temperature of 60°C resulting in a yield of 96%.

These differences are determined by the amount of catalyst, temperature and reaction time when making biodiesel. If the amount added is too small, the reaction will be slow and take a long time. In addition, at a high reaction temperature, the yield of biodiesel produced will increase, but if the reaction has reached an optimum temperature, increasing temperature will reduce the product produced [13].

In this research, biodiesel quality was tested regarding viscosity, density, acid number and flash point. The density obtained by biodiesel was 879 kg/m3, still considered good in consideration to that the density range contained in SNI is in the range of 850 kg/m3 to 890 kg/m3. Meanwhile, the viscosity obtained was 6.1cst, which is not included in the SNI range, where the SNI range is in the range of 2.3 to 6.0cst. This was due to the separation (settling) being less effective and imperfect. In addition, impurities still present in biodiesel after separation increased the viscosity of biodiesel. These impurities can be glycerol and polar monoglycerides (soluble in glycerol) compared to biodiesel [14].

Acid number refers to the main factor when making biodiesel. The higher the acid number, the more corrosion is caused and can damage the diesel engine [14,15]. In this study, an acid number obtained was 0.5, included in the SNI standard. Flash point is the lowest temperature of a substance (fuel) at which sufficient vapor can be formed and form a flammable mixture in air, and can ignite briefly if exposed to an external heat source or flame. In this study, the flash point of biodiesel was 174°C and it is still suitable with SNI in which the minimum flash point is 100°C.

4. Conclusion

From this research, it can be concluded that the activated carbon from palm kernel shells can be used as a catalyst as it could meet standard of SNI 06-3730-1195 from tests for volatile matter content, ash content and water content. The higher KOH concentration during the impregnation process, the higher the ability to absorb potassium metal. The best condition for the concentration and impregnation time for the absorbed potassium metal was found from 5 N at 21 hours with a value obtained of 25.4570%. Meanwhile, the biodiesel obtained was found in accordance with SNI 06-3730-1195 in the density test, acid number and flash point.

References

[1] F.P. Perdani, C.A. Riyanto, Y. Martono, Karakterisasi karbon aktif kulit singkong (manihot esculenta crantz) berdasarkan variasi konsentrasi H3PO4 dan lama waktu aktivasi, Ind. J. Chem. Anal., 4 (2021) 72.

[2] S.R. Br Ginting, D. Daniel, N. Hindryawati, Impregnasi natrium hidroksida pada karbon aktif cangkang jengkol sebagai katalis dalam pembuatan biodiesel, Proceedings of the National Chemistry Seminar, Samarinda: (2017). pp. 143-147.

[3] E. Permana, I. Cristine, S.D.S. Murti, F.M. Yanti, Preparasi dan karakterisasi katalis Cu/Zno dengan support karbon aktif menggunakan aktivator H_3PO_4 dan $ZnCl_2$", ICAJ, 13 (2020) 6-15.

[4] S.Z. Naji, C.T. Tye, A.R. Mohamed, Biofuel production via catalytic cracking of waste cooking oil using sulfonated activated carbon supported La/Ce bimetallic catalysts, IOP Conf. Ser.: Mater. Sci. Eng., 1257 (2022) 012008.

[5] Yuliusman, A. Diana, Adsorption of carbon monoxide (CO) gas and

clearing fire smoke using activated carbon from coconut, The 13th International Conference on QIR, Quality in Research (2013) pp. 496-503.

[6] L. Efiyanti, S.A. Wati, M. Maslahat, Pembuatan dan analisis karbon aktif dari cangkang buah karet dengan proses kimia dan fisika, J. For. Sci., 14 (2020).

[7] S. Huda, D. Ratnani, Laeli, Karakterisasi karbon aktif dari bambu ori (bambusa arundinacea) yang di aktivasi menggunakan asam klorida (HCl), Journal of Inovasi Teknik Kimia, 5 (2019) 22-27.

[8] M. Zamhari, Yuniar, D.I. Sari, N.S. Saputri, Catalyst heterogeneus base production from acacia wood dust, KINETIKA, 10 (2019) 38–45.

[9] Taslim, O. Bani, Iriany, N. Aryani, G.S. Kaban, Preparation of activated carbon-based catalyst from candlenut shell impregnated with KOH for biodiesel production, KEM, 777 (2018) 262–267.

[10] A.O. Etim, E. Betiku, S.O. Ajala, P.J. Olaniyi, T.V. Ojumu, Potential of ripe plantain fruit peels as an ecofriendly catalyst for biodiesel synthesis: optimization by artificial neural network integrated with genetic algorithm, Sustainability, 10 (2018) 707.

[11] C.C. Cardoso, A. S. Cavalcanti, R.O. Silva, S.A. Junior, F.P. de Sousa, V.M. D. Pasa, S. Arias, J.G.A. Pacheco, Residue-based CaO heterogeneous catalysts from crab and mollusk shells for FAME Production Via Transesterification, J. Braz. Chem. Soc., 31 (2020) 756–767.

[12] B. Narowska, M. Kułażyński, M., Łukaszewicz, E. Burchacka, Use of activated carbons as catalyst supports for biodiesel production, Renew. Energy, 135 (2019) 176–185.

[13] T. Susanti, S. Santosa, Studi penggunaan katalis CaO-NaOH pada produksi biodiesel dari minyak jelantah, DISTILAT: Journal of Teknologi Separasi, 8 (2022) 294-300.

[14] D.P. Silaban, A.K. Makalalag, Minyak jelantah production and characterization biodiesel from used cooking oil, J. Penelit. Teknol. Ind. 12 (2020) 31-40.

[15] D. Khoiruummah, N. Sundari, M. Zamhari, S. Yuliati, Aplikasi katalis berbasis karbon aktif dari kayu akasia (acacia mangium) diimpregnasi basa pada sintesis biodiesel, Proceedings of Chemical Engineering Student Seminar, 1 (2020).