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Iron Impregnation on Activated Carbon Prepared from Tamarind Wood (*Tamarindus Indica L.*) as a Potential Catalyst in Biodiesel Production

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Abstract

Renewable energy in the form of biodiesel requires a process called transesterification. This process runs slowly, so a catalyst is needed to reduce the activation energy and speed up the reaction rate. Activated carbon is one of the supports in transesterification catalysts because of its high surface area and is proven to be effective in gas or liquid phase reactions. This work aims to study the potential of active carbon from tamarind wood for making catalysts, the characteristics of the catalyst and the optimal concentration of $Fe(NO_3)_3$ in the impregnation step. Activated carbon was impregnated using an Ultrasonic Processor with 80% strength at 60 °C for 60 minutes. The impregnation process was carried out with variations of 2, 4, and 6% $Fe(NO_3)_3$ dissolved in 0.09M isopropyl alcohol. Variation of processing time 30, 40, 50, 60, 70, 80 minutes. Furthermore, after the activated carbon is allowed to stand for 24 hours, a calcination process is carried out at 300°C to remove impurities. Obtained materials have been characterized by SEM and XRD. The Fe-impregnation process has been successfully carried out on activated carbon made from Tamarind wood (*Tamarindus indica L.).* In the Fe precursor solution concentration range of 2 – 6%, the higher the concentration of the Fe precursor solution, the higher the impregnated Fe metal. Fe-impregnated activated carbon has the characteristics of being a material consisting of a mixture of crystalline and amorphous phases with even porous surface morphology. This Fe-impregnated activated carbon is a potential material as a catalyst in the biodiesel production process.

INTRODUCTION

In a situation where world energy reserves are increasingly limited, energy consumption in the world is increasing, especially petroleum fuels. To overcome the scarcity of petroleum fuel, alternative energy sources are needed, including switching to bioenergy. Now a lot of research has been carried out to produce renewable fuels derived from vegetable oils known as biofuels (Wahyuni et al., 2011).

Biodiesel is a biofuel, a renewable fuel that will not run out as long as the raw material is available. Biodiesel is environmentally friendly because it does not contain SO_2, thereby reducing emissions (Atmoko et al., 2014). Biodiesel is obtained from vegetable oil by converting triglycerides into methyl esters through a transesterification process (Astuti & Mufrodi, 2019). Biodiesel can be produced from vegetable oil i.e. palm oil, jatropha and microalgae (Rajpoot et al., 2023), sunflower and castor oil (Foroutan et al., 2023), soybean oil (Sarkar et al., 2023; Yusuf et al., 2023), coconut oil (Mendez et al., 2022) and from waste cooking oil (Astuti el al., 2023a). The transesterification process of vegetable oil is a slow reaction, so it requires a catalyst to reduce the activation energy and speed up the reaction rate.

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The speed of the reaction rate in the transesterification process can be influenced by the use of an acid or base catalyst. The catalyst most often used in this process is a base catalyst (Hartono et al., 2023)

According to Satterfield (1980), the easiest way to prepare catalysts used in transesterification reactions is through the impregnation method. Impregnated catalyst products are easy to use and have a large surface area of active components due to diffusion. In general, impregnation is divided into two types, namely the carrier metal and metal salt which are mixed simultaneously or the mixture of carrier and metal salt added alternately (Augustine, 1996).

Activated carbon is one of the supports in transesterification catalysts because of its large surface area and has been proven to be effective in gas and liquid phase reactions. Activated carbon itself is a porous material with a carbon content of 87-97% and a small amount of hydrogen and oxygen bound to functional groups, so it can influence the surface absorption properties of activated carbon. Activated carbon as a supporting material ensures the catalyst works more efficiently (Murti, 2008). The source of activated carbon itself can be obtained from sawdust, bricks, coconut shells and wood. One carbon source is the wood of the Tamarind tree (*Tamarindus indica L.*) which is easy to obtain and is usually planted along rural roads. This tree belongs to a monotropic genus and comes from the subfamily *Caesalpinioideae* with *Leguminosae (Fabaceae)* (Nasir, 2019). Tamarind wood contains high carbon elements.

Iron metal (Fe) from the $Fe(NO_3)_3$ precursor solution can be impregnated on activated carbon as support and used as a neutral heterogeneous catalyst in the transesterification reaction. The purpose of the self-impregnation method is to fill the pores of the activated carbon with a metal salt solution and appropriate concentration to achieve the correct loading. Wang et al. (2022) used bifunctional Na-Fe-Ca nano catalyst to produce biodiesel at low temperature.

Catalysts are produced through several stages, namely the drying and calcination stages, where the catalyst is dried after impregnation so that the water evaporates and salt crystals can form on the surface of the activated carbon. Drying speed influences the formation of salt crystals in the middle of the carrier particles or at the bottom of the substrate pores. The drying rate affects the temperature gradient which increases and causes the salt crystals to migrate out of the pores. The calcination process is carried out under optimal drying conditions to convert the salt into its oxide (Ginting et al., 2017).

Heterogeneous catalysts are used because metal alloys made from supporting materials help the catalyst work more selectively and efficiently. In previous research, data was obtained regarding the process of modifying activated carbon as a supporting material to be used as a catalyst in the biodiesel production process (Astuti et al., 2023a). This research focuses on testing catalysts that have been produced in previous research. Impregnation is a treatment with various mixtures of active metals in solution. Metal salts will enter the carbon pores during the impregnation process (Putri, 2014).

According to Yusnani (2008), there are four general steps for making catalysts, namely drying, calcination, oxidation and reduction. Drying aims to reduce solvent levels by means of heat treatment. Calcination is a heat treatment process in a furnace at high temperatures (Hakim et al, 2019). According to Siregar (2020), catalyst impregnation is a method used to insert a metal catalyst into a supporting material or porous medium so that the metal's active sites can be evenly distributed throughout the surface and pores of the supporting material.

Impregnation is a method of complete saturation of a certain substance. This is done by filling the pores of the buffer with an active metal solution through metal adsorption. The method is like soaking the support in a solution containing active metal. Impregnation is carried out on a support that does not contain anions or cations exchanged in the active phase. The metal impregnation process is carried out by adding supporting materials to the metal precursor solution which is stirred by heating it below the boiling point of the solvent until it forms a slurry (Yuhermita et al., 2021). Dewi et al. (2016) stated that impregnation is suitable for catalysts with a relatively small weight percent of active components, with active components in noble metals such as platinum. Through impregnation, it is hoped that the metal components can be distributed perfectly so that a fairly large surface area with active components is obtained.

Biomass such as wood can be used as raw material for making catalysts. Previous research (Astuti et al., 2023b) explained that active carbon

can be made from Javanese tamarind charcoal. This research aims to determine the potential of active carbon from tamarind wood as catalysts, the influence of $Fe(NO_3)_3$ concentration in the impregnation step, and the characteristics of the catalyst produced.

MATERIALS AND METHOD

Equipments

This research uses an ultrasonicator as the main equipment. The ultrasonic processor used in this research has a power of 220 V, single phase type, power adjustment range 0-100%, temperature range 0-300°C, time range of 1 second - 99 hours, and tool dimension specifications: Chamber: 270mmx240mmx400mm; Control Boxes: 365mm x 235mm x 215mm; and Ultrasonic Head: 425 mm.

Materials

The materials used in this study was aquadest from UD Organik, Fe(NO3)3.9H2O. of ≥ 98% purity from Labo Chemie PVT.LTD., hydrogen chloride (HCl) of 37% from Merck, and isopropyl alcohol of ≥ 99.8% purity from Supelco. Tamarind charcoal is obtained from a joss coffee charcoal supplier.

Methods

Catalyst preparation was carried out by impregnating activated carbon from Tamarind wood (*Tamarindus indica L.*) with $Fe(NO_3)_3$ solution. Before impregnation, activated carbon was activated with 4M HCl to make the carbon more acidic and also to reduce the impurities in the carbon. Next, the acidified carbon was neutralized until the pH becomes 7 and dried at a temperature of 110°C. A total of 5 grams of 60 mesh sized active carbon was mixed with 2%, 4% and 6% $Fe(NO_3)_3$ solutions. The iron metal precursor solution was made by dissolving solid $Fe(NO_3)_3.9H_2O$ in 10 mL of 0.09 M isopropyl alcohol. This sample was impregnated using an Ultrasonic Processor with a temperature of 60°C, the power used was 80%, and with time variations of 30, 40, 50, 60, 70, 80 minutes. The catalyst will dry slowly over 24 hours at room temperature. After the catalyst was dry, the calcination process was carried out at a temperature of 300°C for 3 hours. Characterization of impregnated activated carbon was carried out using Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD).

RESULTS AND DISCUSSION

The sample used in the first SEM analysis was an activated carbon sample that has been activated with a 4M HCl solution without (before) impregnation. Figure 1 shows that activated carbon has an overall porous surface morphology and spreads evenly. Analysis of the mapping of metal elements contained in activated carbon before impregnation is shown in Figure 2.

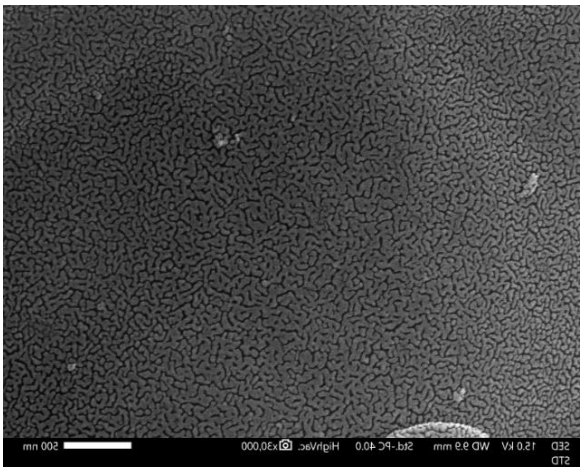


Figure 1. Micrograph of activated carbon surface morphology before impregnation.

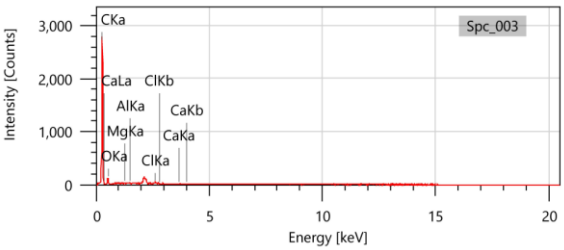


Figure 2. Content of several chemical elements in activated carbon before impregnation.

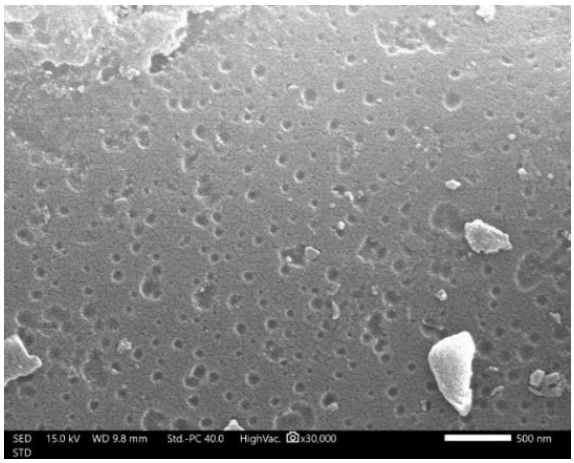
Table 1. Elemental components of activated carbon.

Element	line	Mass%	Atom%
C	K	87.89±0.36	91.06±0.38
O	K	10.99±0.42	8.54±0.33
Mg	K	0.10±0.03	0.05±0.02
Al	K	0.07±0.03	0.03±0.01
Cl	K	0.50±0.05	0.18±0.02
Ca	K	0.45±0.07	0.14±0.02
Total		100.00	100.00
Spc_003		Fitting ratio 0.0498	

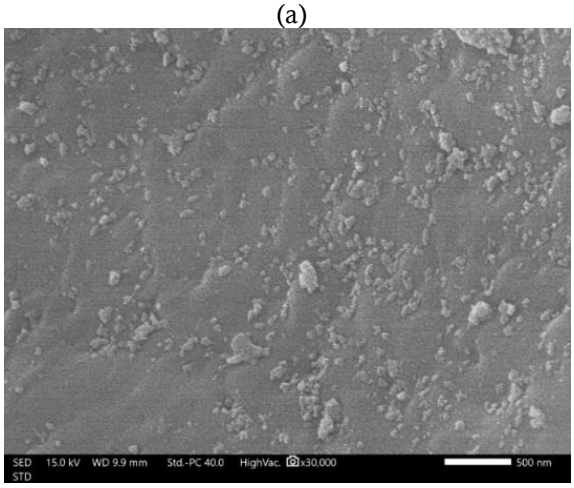
Activated carbon before impregnation contains carbon (C), calcium (Ca), chloride (Cl), aluminum (Al), magnesium (Mg), and oxygen (O).

Quantitatively, the amount of metal elements contained in activated carbon is presented in Table 1.

Based on Table 1, the amount of carbon is 87.89 ± 0.36% by mass as the main constituent of the supporting material. The second highest element content is oxygen at 10.99 ± 0.42%. The levels of other elements such as Mg, Al, Ca, and Cl are below 1% by mass. Activated carbon samples before impregnation do not contain Fe metal elements. Figure 3 shows a micrograph of the surface morphology of activated carbon samples impregnated using $Fe(NO_3)_3$ with Fe content of 2% and 6%.



(a)



(b)

Figure 3. Surface micrograph of activated carbon impregnated with (a) 2% Fe and (b) 6% Fe.

In Figure 3(a) it is shown that the 2% Fe-impregnated activated carbon catalyst has several pores on the carbon surface which are covered by Fe metal elements, but not evenly distributed over the entire surface. In Figure 3(b) the surface morphology of the impregnated activated carbon catalyst sample is shown. 6% Fe, all of the pores of which are closed by the metallic element Fe. This shows that the greater the concentration of $Fe(NO_3)_3$ used in the impregnation process, the more Fe metal elements are contained on the carbon surface.

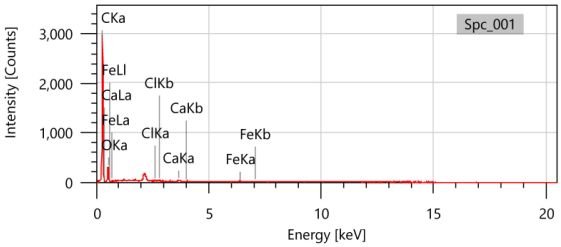


Figure 4. Content of several chemical elements in activated carbon impregnated with 2% Fe.

The number of elements contained in activated carbon is presented in Figure 4 and indicated by the resulting peak graph. Quantitatively, the content of several chemical elements contained in impregnated activated carbon is presented in Table 2.

Table 2. Elemental content in activated carbon impregnated with 2% Fe

Element	line	Mass%	Atom%
C	K	76.37±0,31	82.23±0.34
O	K	21.15±0,47	17.09±0.38
Cl	K	0.43±0.04	0.16±0.02
Ca	K	0.47±0.06	0.15±0.02
Fe	K	1.58±0.17	0.37±0.04
total		100.00	100,00
Spc_001		*Fitting ratio* 0.0533	

Table 2 shows that C content is 76.37 ± 0.31% by mass. The oxygen element content is 21.15 ± 0.47% by mass. The Fe element content impregnated is 1.58 ± 0.17% by mass. The existence of the Fe metal element shows the success of impregnation of Fe metal on the surface of the activated carbon. Meanwhile, the Cl and Ca elements contain less than 1% by mass.

In Figure 5, the results of mapping the metal elements contained in activated carbon are presented after impregnation with a $Fe(NO_3)_3$ concentration of 6%.

The elements contained in the catalyst sample include carbon (C), iron (Fe), oxygen (O), magnesium (Mg), calcium (Ca) and chloride (Cl). The element with the highest peak is carbon as the

main element. Furthermore, the calcium peak is below the carbon peak, and at the third peak there is the element iron. Quantitatively, the chemical elements contained in activated carbon impregnated with 6% Fe can be seen in Table 3.

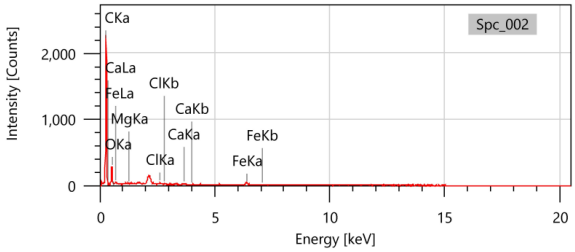


Figure 5. Content of several chemical elements in activated carbon impregnated with 6% Fe.

Table 3. Chemical element content in 6% Fe-impregnated activated carbon.

Element	line	Mass%	Atom%
C	K	73.07±0.34	80.79±0.37
O	K	21.42±0.50	17.78±0.41
Mg	K	0.18±0.04	0.10±0.02
Cl	K	0.27±0.04	0.10±0.02
Ca	K	0.23±0.06	0.08±0.02
Fe	K	4.83±0.29	1.15±0.07
Total		100.00	100.00
Spc_002		*Fitting ratio* 0.0612	

The content of the main element carbon (C) is 73.07 ± 0.34%. The oxygen element content is 21.42 ± 0.50% by mass. The Fe element content is 4.83 ± 0.29% by mass. This shows that Fe metal has been successfully impregnated on the surface of the activated carbon material, although not all of the Fe from the precursor solution can be impregnated.

Crystallinity

In this study, XRD was used to identify the crystallinity phase of the impregnated activated carbon. The samples used in this test were carbon samples containing 2% and 6% Fe which were impregnated for 60 minutes at a temperature of 60°C.

Figure 6 shows the x-ray diffractogram pattern of iron-impregnated activated carbon, which generally consists of two broad peaks at around 23.5° and 44° 2θ respectively. The first peak is the characteristic peak of active carbon, while the next peak is the peak of Fe metal contained in active carbon. This relatively wide diffractogram peak can be interpreted to mean that Fe-impregnated activated carbon is a material consisting of crystalline and amorphous phases. The results of peak area measurements at 23.5° 2θ showed crystal formation of 27.5% for activated carbon impregnated with 6% Fe and 33.7% for samples impregnated with 2% Fe. Figure 6 explains that the increasing concentration of Fe(NO3)3 causes more Fe metal to be impregnated. The resulting catalyst is a material that is a mixture of crystalline and amorphous phases with a uniformly porous surface. The results of this impregnation have the potential as a catalyst in biodiesel production.

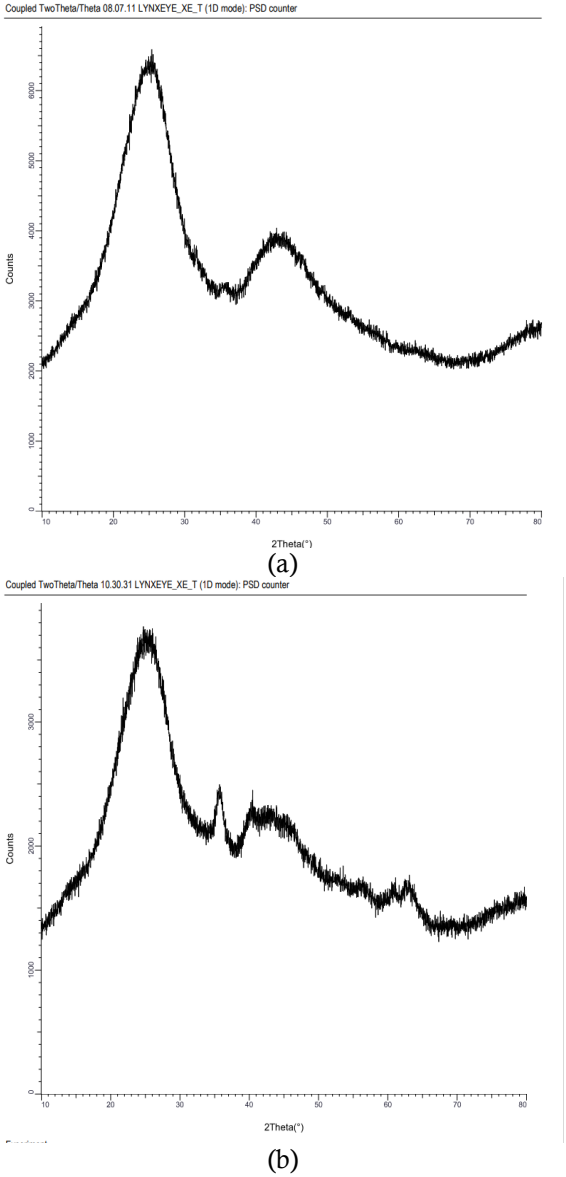


Figure 6. X-ray diffractogram pattern of activated carbon impregnated with (a) 2% Fe and (b) 6% Fe.

CONCLUSION

The Fe-impregnation process has been successfully carried out on activated carbon made from Tamarind wood (*Tamarindus indica L.).* In the Fe precursor solution concentration range of 2 – 6%, the higher the concentration of the Fe precursor solution, the higher the impregnated Fe metal. Fe-impregnated activated carbon has the characteristics of being a material consisting of a mixture of crystalline and amorphous phases with even porous surface morphology. This Fe-impregnated activated carbon is a potential material as a catalyst in the biodiesel production process. Experiments on making biodiesel from vegetable oil with a Fe-impregnated activated carbon catalyst are underway.

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