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Synthesis of SnO_2 Using Hydrothermal Method and Its Application as Catalyst in Esterification of Oleic Acid

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Abstract

Biodiesel is currently getting great attention because it can reduce carbon dioxide emissions by 78.5% compared to petroleum-based diesel. The reaction that can produce biodiesel is the esterification reaction with the addition of a heterogeneous catalyst, one of which is SnO_2 which can be used as Lewis acid for the esterification reaction. In our study, SnO_2 has been successfully synthesized and then succeeded in reducing the level of oleic acid FFA (Free Fatty Acid) through an esterification reaction. SnO_2 was synthesized from $SnCl_2.2H_2O$ using the hydrothermal method with the addition of CTAB (Cetyl Trimethyl Ammonium Bromide) as a capping agent which was then analyzed using XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscopy). The catalytic activity of the SnO_2 sample was carried out through the esterification reaction of oleic acid in ethanol at 65 °C for 6 hours with variations in catalyst weight and variations in the ethanol mole ratio. From XRD analysis, SnO_2 sample consists of cassiterite minerals and has typical peaks at 2θ = 26.56°; 33.84°; 37.92°; 38.90°; 42.53°; 51.64°; 54.66°; 57.76°; 61.68°; 62.34°; 64.60°; and 65.88° with the highest intensity at 2θ = 33.84°. During condition optimization of esterification reaction of oleic acid, variations in the weight of SnO_2 catalyst resulting from the optimum FFA level could be reduced by 75.05%, whereas to variations in the mole ratio of ethanol, the optimum FFA level could be reduced by 85.53%. In our study, SnO_2 has been successfully synthesized and then succeeded in reducing the level of oleic acid FFA through esterification reaction until 85.53%.

Keywords: *Esterification; Oleic Acid; SnO_2; Hydrothermal; Catalyst.*

Introduction

Biodiesel has recently received great attention, it has been reported that pure biodiesel can reduce carbon dioxide emissions by 78.5% compared to petroleum-based diesel (Sheehan et al. 1998). The high amount of biodiesel cetane results in good combustion properties. Besides that, biodiesel has other advantages such as low sulfur content, low pollution, and good lubrication performance (Li et al. 2014). These factors cause biodiesel to be considered a green and renewable energy source (Li et al. 2014). Biodiesel can be produced from the esterification reaction between oleic acid and ethanol in which a catalyst is added to speed up the reaction.

The catalyst used is usually an acid homogeneous catalyst such as sulfuric acid, but its use cannot be taken into account because it produces toxic waste and pollutes

the environment (Li et al. 2014). Therefore, in recent years, there has been a lot of research on heterogeneous catalysts that can be used to replace sulfuric acid as a homogeneous catalyst in esterification reactions such as solid heteroacids, heteropoly acids, or cation-exchange resins with strong acidity thereby solving problems such as it is corrosive, produces toxic waste, and pollutes the environment (Li et al. 2014). However, the manufacture of these catalysts is relatively complicated and the costs of their products are very expensive. Therefore, it is necessary to develop new environmentally friendly and efficient catalysts for biodiesel synthesis by the esterification reaction.

Tin (Sn) is an important concern because it can be used as a Lewis acid for esterification reactions and shows high catalytic activity (Cardoso, Neves, and Da Silva 2008). One of them is SnO_2 which can be obtained from various methods such as precipitation, sonochemical, sol-gel, and hydrothermal (Cardoso et al. 2008)(Setiadji et al. 2017)(Setiadji et al. 2018). The method that is often used is the hydrothermal method because of its simplicity and the possibility to modify the desired particle size, morphology, and degree of crystallinity based on the experimental procedure (Doyle; Albayati M Talib; Abbas; Alismaeel 2016).

It has also been reported that the SnO_2/WO_3 catalyst in biodiesel synthesis can reduce the FFA (Free Fatty Acid) levels in oleic acid by 47-90% (Sarkar, Ghosh, and Pramanik 2010). The decrease in FFA levels was caused by the ratio between the weight of the catalyst and the ethanol used, where the more ethanol used, the higher the decrease in FFA levels (Sarkar et al. 2010).

Therefore, in this study, the SnO_2 synthesis process was carried out using the hydrothermal method with $SnCl_2.H_2O$ as a precursor and CTAB (Cetyl Trimethyl Ammonium Bromide) as a template that will direct the formation of crystal structures with the size of nanoparticles. The results from the synthesis of SnO_2 will be characterized using XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscopy) which will be applied as a catalyst in the esterification reaction of oleic acid and ethanol using the variations in the weight of the SnO_2 catalyst and variations in moles of ethanol to see the effect on reducing FFA levels in oleic acid.

Methods

In this study, the synthesis of SnO_2 from $SnCl_2.H_2O$ was implemented by using CTAB (Cetyl Trimethyl Ammonium Bromide) with the hydrothermal method. After obtaining SnO_2, it was characterized using XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscopy) and applied as a catalyst in the esterification reaction of oleic acid with ethanol.

Materials

The materials used in this study were $SnCl_2.2H_2O$ (Merck), DM water, CTAB (Merck), ammonium hydroxide (NH_4OH) (25%), ethanol (98%), oleic acid, KOH (Merck), and phenolphthalein.

Characterization

The crystallinity of SnO_2 was determined using X-ray diffraction (XRD) analysis (Philips PW 1030 X-Ray Diffractometer), while the morphology of SnO_2 was determined using a Scanning Electron Microscope (SEM) (JEOL JSM 6510).

Procedure

Synthesis of SnO_2

The synthesis of SnO_2 refers to research conducted by Sathishkumar et al (Sathishkumar, S., Parthilbavarman, M., Sharmila, V., & Karthik 2017). 2.25 grams of $SnCl_2.2H_2O$ dissolved in 10 mL of DM water. Then, 1 gram of CTAB was added while stirring with a magnetic stirrer for 15 minutes. Afterward, NH_4OH has added to pH 10. The resulting sol is washed with water and ethanol to pH 7. Then the sol is transferred to an autoclave and put in an oven at 180 °C for 12 hours, the resulting precipitate is washed with aqua DM to pH 7 and then dried in an oven at 105 °C for 10 hours. The dry precipitate is then calcined at 600 °C for 3 hours.

Esterification Reaction of Oleic Acid

This biodiesel synthesis refers to the research of Doyle et al (Doyle; Albayati M Talib; Abbas; Alismaeel 2016). Oleic acid: ethanol: SnO_2 in a ratio (1 mol: 6 mol: 1% w/w). 0.2 grams of SnO_2 and 19.5436 grams of ethanol are put in a three-neck flask (a condition in a reflux system) and stirred until the temperature reaches 65°C. After the temperature reaches 65°C, 20 grams of oleic acid are added to it. The mixture was refluxed. A small amount of mixture was taken and put into a 5 mL falcon tube then centrifuged for 3 minutes at a speed of 3000 rpm (the mixture was taken every 1 hour along a reaction time of 6 hours). After that, the solution of the centrifuged mixture was put into Erlenmeyer (weight of the mixture has been obtained) then added five drops of phenolphthalein indicator and titrated with 1 M KOH solution (KOH solution has been standardized) until it turned pink.

The treatment above was also implemented for several variations in ratio of oleic acid: ethanol: SnO_2, including (1 mole : 6 mole : 1% w/w), (1 mole : 6 mole : 5% w/w), (1 mole : 6 mole : 7.5% w/w), (1 mole : 12 mole : 1% w/w), and (1 mole : 15 mole : 1% w/w). For the needs of the titration process, the 1 M KOH solution has been standardized by a 1 M oxalic acid solution. FFA can be calculated using the formula FFA = $(M_{KOH} \times V_{KOH} \times Mr_{KOH})/W_{sample}$. The reduction of the free fatty acid (FFA) level of oleic acid can be calculated using the formula % (percent) conversion of FFA = [(initial FFA – final FFA) / initial FFA] x 100%.

Results and Discussion

Characterization of SnO_2

Analysis using XRD was implemented to identify the crystal structure of the SnO_2 sample. This XRD analysis used CuKα radiation with a wavelength of 1.5406 Å. Figure 1 shows that the SnO_2 sample consists of cassiterite minerals and has typical peaks at 2θ between 27-66°, namely at 2θ = 26.56°; 33.84°; 37.92°; 38.90°; 42.53°; 51.64°; 54.66°; 57.76°; 61.68°; 62.34°; 64.60°; and 65.88° with the highest intensity at 2θ = 33.84° (Sathishkumar, Parthilbavarman, Sharmila, & Karthik, 2017).

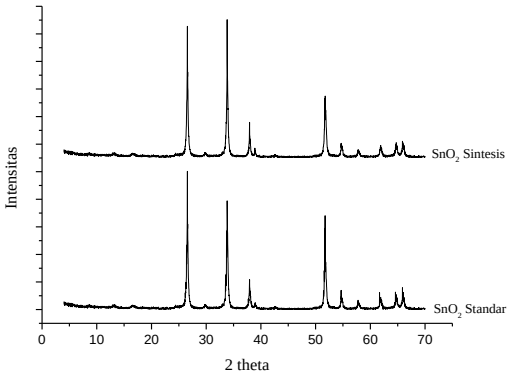

Figure 1 XRD pattern of (a) SnO_2 standard and (b) SnO_2 sample

From XRD analysis, the average crystal diameter is obtained from calculations based on the Debye Scherrer equation, ($D = k.\lambda / \beta.\cos\theta$), with the value obtained, namely 3.43 nm.

According to the XRD pattern in Figure 1, it can be seen that there is no peak shift in the pattern of synthesized SnO_2 when compared to the SnO_2 standard. The crystal structure of the synthesized SnO_2 is a tetragonal crystal structure which is the structure of SnO_2 standard. This indicates shows that SnO_2 was successfully synthesized via the hydrothermal method.

The synthesized SnO_2 was characterized using SEM with a surface magnification of 10,000 times as shown in Figure 2. According to the analysis using SEM, it can be seen the average particle size of the synthesized SnO_2. The SEM results in the form of photos are processed using the ImageJ application. The results obtained that an average particle size of SnO_2 is 5.51 nm.

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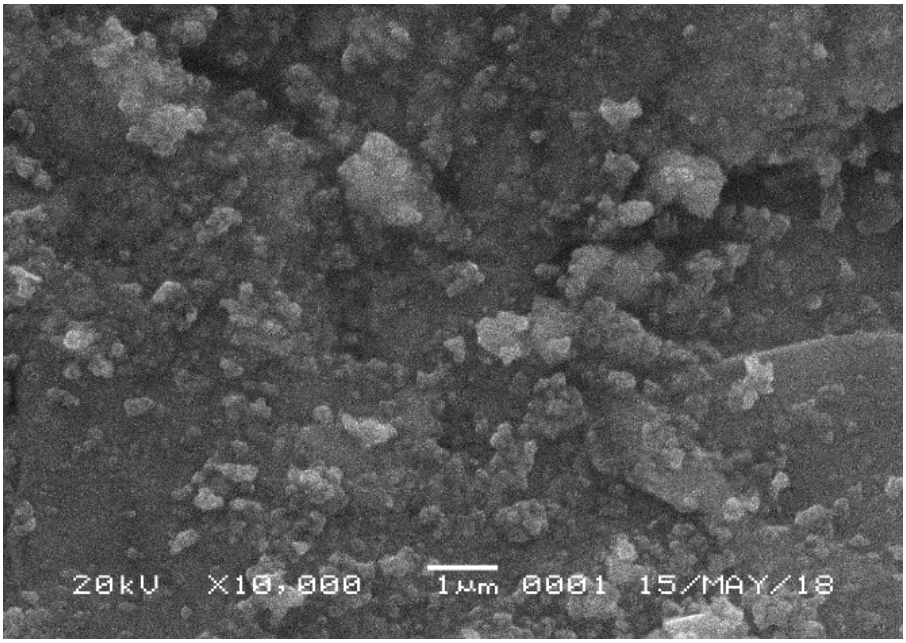

Figure 2 SEM Photos of Synthesized SnO_2

The catalytic activity of SnO_2

The synthesis of biodiesel in this study was implemented by the esterification reaction of oleic acid using the synthesized SnO_2 as a catalyst to determine the decrease in FFA levels in oleic acid. The oleic acid esterification reaction is applied using ethanol. Firstly the water content in the oleic acid has been removed when will be used so that it does not interfere with the esterification process. As for identifying FFA content in the oleic acid after esterification reaction done through a titration using the KOH 1 M as a titrant and the phenolphthalein indicator as a determinant of the endpoint of the titration.

To identify the percent initial levels of FFA in the oleic acid used for the esterification reaction, it was implemented by mixing 3 g of oleic acid and 30 g of ethanol, both of which are put into Erlenmeyer and then titrated using 1 M KOH. Before being titrated into it, 5 drops of phenolphthalein were added to determine the endpoint of the titration. In our work, the initial FFA levels contained in oleic acid based on the analysis and calculation results were 291.5803%.

The esterification reaction was conducted with varying the mole ratio of oleic acid: ethanol: catalyst, respectively. For variations of the catalyst weight, the mole ratios used are (1 mole : 6 mole : 1% w/w), (1 mole : 6 mole : 5% w/w) and (1 mole : 6 mole : 7.5% w/w). For variations of the ethanol mole, the mole ratios used are (1 mole : 6 mole : 1% w/w), (1 mole : 12 mole : 1% w/w) and (1 mole : 15 mole : 1% w/w). This variation of the mole ratio aims to find the optimum condition of the esterification process that is related to the reduction of FFA levels of oleic acid.

As a comparison, this study also conducted an esterification reaction without a catalyst to determine the decrease in FFA levels in oleic acid. This reaction was implemented by mixing oleic acid with ethanol at 65 °C using the reflux method. The result showed that the final FFA level was 286,116% which showed a decrease of only 1,874%.

Furthermore, the esterification reaction was implemented using a catalyst with a mole ratio of oleic acid: ethanol: catalyst (1 mole: 6 mole: 1% w/w), respectively. The steps included weighing 19.5436 g of ethanol (6 x mole of oleic acid x Ar ethanol) and 0.2 g of SnO_2 (1% x weight of

oleic acid) which were mixed in a three-neck flask and stirred so that all components were mixed homogeneously while refluxed until the temperature reached 65 °C. After the temperature reaches 65 ° C, 20 g of oleic acid were added into a three-neck flask and the temperature was kept at 65 °C.

To determine the decrease in FFA levels of the mixture, it was taken every 1 hour along with 6 hours of reaction time. Titration was implemented using 1 M KOH solution dan phenolphthalein indicator. The endpoint of the titration is indicated by a color change from clear yellow to pink. Furthermore, for the variation of (1 mol : 6 mol : 5% w/w), (1 mol : 6 mol : 7.5% w/w), (1 mol : 12 mol : 1% w/w), and (1 mol : 15 mol : 1% w/w) is conducted by the same process.

Table 1 shows the conversion of FFA of oleic acid toward variations in the weight of the catalyst. It can be seen that at 1% w/w the conversion of FFA was achieved was 73.71%, at 5% w/w was 75.05%, and at 7.5% w/w was74.69%, each of which has the optimum reaction time at 360 minutes. In our work, FFA conversion by SnO_2 yielded almost the same value for the three weight variations of the catalyst. Increasing the amount of catalyst used and of the reaction time will increase the conversion FFA value of oleic acid. The ratio of 1% of catalyst weight gives a high value of FFA conversion so that this ratio of catalyst weight is then used as a fixed variable for the variation of moles of ethanol.

Table 1. Conversion of FFA of oleic acid with the variation of SnO_2 catalyst weight

Reaction Times (Minutes)	Conversion of FFA (%)		
	The ratio of oleic acid: ethanol: catalyst		
	1:6:1%	1:6:5%	1:6:7.5%
20	70.83	71.89	70.68
40	71.24	72.19	71.34
60	72.42	73.26	73.19
120	72.95	74.18	73.47
180	73.13	74.54	74.20
240	73.01	74.09	73.64
300	73.41	74.75	73.68
360	73.71	75.05	74.69

1% of catalyst weight is used in the esterification reaction with variations in the mole ratio of ethanol 6, 12, and 15. Table 2 shows that the FFA conversion values have a significant difference for the three-mole ethanol variations. It can be seen that at 6% of mole ratio of ethanol the conversion of FFA was 73.21%, at 12% of mole ratio of ethanol was 82.89%, and at 15% of mole ratio of ethanol was 85.53%, each of which is optimum at a reaction time of 360 minutes. Increasing the amount of ethanol will shift the reaction equilibrium going to the product and the ability of the catalyst will increase the selectivity leading to the main product.

Table 2. Conversion of FFA of oleic acid with the variation of ethanol mole

Reaction Time (Minutes)	Convert Acid Number (%)		
	The ratio of oleic acid: ethanol: catalyst		
	1:6:1%	1:12:1%	1:15:1%
20	70.83	80.24	83.12
40	71.24	80.61	83.89
60	72.42	80.81	84.09
120	72.95	81.55	84.52
180	73.13	81.65	84.81
240	73.01	82.31	84.85
300	73.41	82.78	84.92
360	73.71	82.89	85.53

In our work, the optimum conditions for the esterification reaction of oleic acid with ethanol catalyzed by SnO_2, namely a composition of oleic acid: ethanol: catalyst at 1 mol: 15 mol: 1% w/w, respectively. It gives a decrease in FFA levels until 85.53% at the reaction time of 6 hours. This shows that the ester compound was produced via an esterification reaction catalyzed by SnO_2, it was higher than the esterification reaction without a catalyst. Besides that, the esterification reaction becomes more effective.

The mechanism of the reaction that takes place during the esterification reaction can be seen in Figure 3. Firstly, the oxygen atom of ethanol attacks the positive charge of carbon carbonyl (C=O) at oleic acid that

causing a double bond of oxygen at carbon carbonyl to become a single bond so its charge is negative partial.

In the presence of an acid catalyst, the OH group in the oleic acid will bind to the acid site of the catalyst to form a water molecule as a by-product. The formation of a by-product is due to the resonance of electrons from the negatively charged oxygen atom so that it returns become double bonds with carbon carbonyl (C=O) to produce ethyl oleate as a product from esterification of oleic acid.

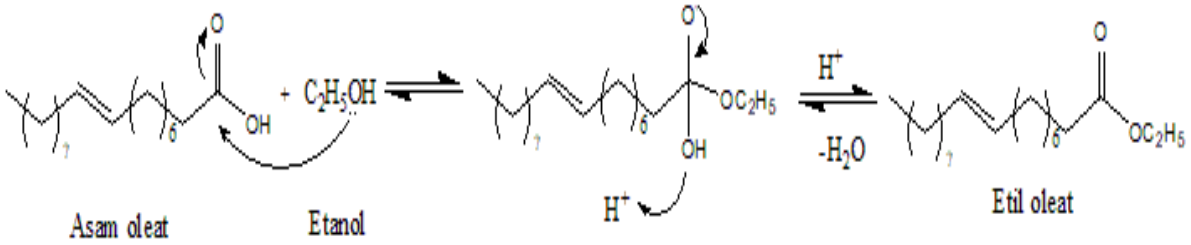

Figure 3. Mechanism of Esterification Reaction of Oleic Acid

Conclusion

According to the XRD results, synthesized SnO_2 has a tetragonal crystal structure and an average crystal diameter of 3.43 nm which was calculated by the Debye Scherrer equation. From the SEM results, it can be seen that the average particle size of SnO_2 is 5.51 nm. SnO_2 was able to reduce FFA levels in oleic acid from an initial FFA of 291.580% became to a final FFA of 42,147%. The greater the mole of ethanol used, the greater the decrease in FFA levels in oleic acid. The optimum reduction in FFA levels was in the variation of the mole ratio of oleic acid: ethanol: catalyst (1:15: 1%), which was 85.53%.

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