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Synthesis and modification of mesoporous silica with sulfated titanium dioxide as a heterogeneous catalyst for biodiesel production from palm fatty acid distillate

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Abstract. This study synthesizes fatty acid ethyl ester (FAEE) through esterification reaction of palm fatty acid distillate (PFAD) using SO_4^{2-}/TiO_2 supported by mesoporous silica as a catalyst. The steps of this study were a synthesis of mesoporous silica, catalyst preparation by impregnation and catalyst activity test through esterification reaction of PFAD by using ethanol. The variables of study on the esterification reaction were the weight ratio of catalyst and PFAD as 3%, 5%, 7%. Based on BET characterization, it shows that synthesized silica material is mesoporous silica. The characterization result of silica and catalyst using X-Ray of wide-angle powder (WAXRD) and SEM gives information that the existence of silica as support of SO_4^{2-}/TiO_2 active site. At the catalyst activity test through esterification reaction, it was obtained the best weight ratio of catalyst and PFAD was 5% with the conversion of ethyl ether formation as 98.9 %. Analysis data and physical properties were viscosity at a temperature of 40 °C and density at the temperature of 15 °C, it shows that the value fit a biodiesel standard of ASTM, meanwhile analysis data of GC-MS toward product of ethyl ester and PFAD has shown that most of the fatty acid in PFAD had been converted into ethyl ester.

1. Introduction

Technology development of biodiesel production faces a new challenge, a higher demand for a clean environment. Previously, biodiesel production used a base or acid liquid (homogeneous) catalyst. Catalyst separation was generally conducted through washing by using water which leads to a high volume of wastewater. Recently solid (heterogeneous) catalyst is widely used to produce biodiesel because it is considered more efficient and more economical and more environmentally friendly. Because it is solid, catalyst separation is easily conducted through filtration.

The study about synthesis and SO_4^{2-}/TiO_2 catalyst usage to produce biodiesel methyl ester (FAME) by using cottonseed oil [1], castor oil [2], jatropha curcas seed oil L. [3]. Based on a study, SO_4^{2-}/TiO_2 is a solid (heterogeneous) catalyst which has high performance in reaction. This property is because metal oxide has good thermal stability, a high specific surface area big size and pore volume [4] besides transitional metal oxide (titanium dioxide, TiO_2) can function as an active site of catalyst because has Lewis acid property. The increase of performance can be conducted by modification by using sulfuric acid. This catalyst was then sulfated so that it is known as a superacid catalyst with good performance and stability if it is used especially for esterification reaction.

However, because of the catalyst particle size is so small and nanomaterial group function (<7,0 nm) it can be the constraint in catalyst separation from product [5]. The solution offered to overcome this problem is by increasing its particle size. The added material is expected simultaneously functioning as support or catalyst matrix. Generally, the material which has to pore such as silica is chosen so that catalyst active site such as metal oxide and sulfonic acid function group can be impregnated on its surface [6].

One option in this study is silica synthesizing which has pore characteristics as mesoporous. It is expected that this silica has potency as a matrix for active sites of SO_4^{2-}/TiO_2. Therefore the catalyst synthesized can be implemented for higher fatty acid feedstock such as palm fatty acid distillate to produce biodiesel (fatty acid ethyl ester). This feedstock is chosen because it consists of fatty acid such as palmitic acid, stearic acid, and oleic acid, which support high-quality biodiesel production.

2. Methodology

2.1 Materials
The materials used in this study were cetyl trimethyl ammonium bromide (CTAB) (Sigma-Aldrich), ludox HS40 (Sigma-Aldrich), triton x100 (Sigma-Aldrich), NaOH (E. Merck), distillate water, acetate acid (E. Merck), HCl (E. Merck), ethanol (E. Merck), H_2SO_4 (E. Merck), titanium dioxide (E. Merck), chloroform (E. Merck) and palm fatty acid distillate (PFAD) obtained from local industry of vegetable oil.

2.2 Equipment
Diffraction pattern of X-Ray(WAXRD) for silica and catalyst was obtained by using radiation of Cu Kα (λ = 1.5406 Å) in diffractometer Bruker D2 Phaser 2nd Gen. The sample was evaluated in a scale of 2θ from 10 to 60 by an increase of 0.02 degree with scanning level of 2^0/minute. The operational conditions were 40 kV and 40 mA.

Analysis of surface area, pore volume and diameter was conducted by using the BET method in an instrument of Quantachrome Touch Win vt.0. Adsorbate model in this instrument is to apply nitrogen gas at a batch temperature of 77.35 K. Morphology characterization was conducted by using SEM for silica synthesis and catalyst synthesis. Analysis to determine the component type in the product was conducted by using GC-MS (GCMS-QP2010 ULTRA SHIMADZU)

2.3 Procedures
2.3.1. Synthesizing Mesoporous Silica. At first, silica solution was made by reacting 14.3 g ludox HS40 solution with 45.25 g NaOH 1 M solution at the temperature of 80^0C in a condition of slightly mixed for 2 hours. Silica solution was then cooled. The next step was surfactant solution was made by mixing 6.12 gram of CTAB with 1.34 gram of Triton x-100, and 83.47-gram distillate water. The mixture was then heated so that the homogeneous surfactant solution is formed. Surfactant solution was then cooled.

The next step was silica and surfactant solution was mixed fast in polypropylene bottle while strongly shaken for 15 minutes. The mixture which was changed the form into gel was then heated in a static condition at the temperature of 100^0C for 24 hours while occasionally shaken. It was cooled at room temperature, 30% acetic acid was added to make the pH up to 10. After that, it was re-heated in a static condition at a temperature of 100^0C for 24 hours. This synthesis method using modified Ryoo method [7]. For the step of purification or removal of the surfactant from the silica, the calcination treatment set at 540^0C for 5 hours.

2.3.2 *Synthesizing Catalyst.* At first, 10 gram of TiO_2 was added with 2 molar of H_2SO_4 and mixed well, it was then added synthesized silica. The weight ratio between TiO_2 to silica was 5:1. This mixture was continuously stirred for 6 hours at a speed of 300 rpm. After that, it was heated in an oven for 24 hours at the temperature of 105^0C it was then calcined in a stove at the temperature of 400^0C for 4 hours.

2.3.3 *Esterification of Palm Fatty Acid Distillate.* At first, a certain amount of PFAD was melted, after being melted, it was fed into the reactor with the temperature of 80$^\mathrm{o}$C with stirring speed set at 250 rpm. After that ethanol was added with molar ratio to PFAD as 13 and solid catalyst with weight ratio to PFAD variation as 7%, 5%, and 3%. After that the reactor was turned on and set as desired operation condition, it was set that the reaction was carried out for 4 hours. The level of unreacted free fatty acid was measured using acid-base titration method by using KOH 0.1 M and ester formation conversion is calculated by using a formula of:

$$\text{Acid value } C = \frac{1000 \cdot V_{KOH} \cdot M_w \cdot N_{KOH}}{W} \tag{1}$$

$$\text{Conversion } X = \frac{C_0 - C_1}{C_0} \times 100\% \tag{2}$$

In which V is volume KOH solution used for titration (mL), Mw is molecule weight of KOH (56.1 g/gmol), N is concentration (gmol/L), W is sample weight (g), Co is acid value before reaction and C_1 is acid value after the reaction.

The best catalyst quantity was determined based on the lowest remaining free fatty acid analysis. The best experimental variation through catalyst weight is determined by the final conversion of ester formation obtained. The physical property of biodiesel was tested based on density analysis at 15$^\mathrm{o}$C and kinematic viscosity at 40$^\mathrm{o}$C

3 Results and Discussion
3.1 Mesoporous Silica and Catalyst Characterization

The procedure of this study was started by synthesizing silica material mesopores and characterizing it. The product of silica was modified by sulfuric acid and titanium dioxide through impregnation method to produce heterogeneous catalyst and was characterized. Catalyst performance was tested in the esterification of palm fatty acid distillate into fatty acid ethyl ester. Silica characterization and catalyst is indicated through the characterization of WAXRD with Bragg angles of 2θ = 10- 60°. Figure 1 below shows the diffraction pattern of X-Ray of wide-angle powder (WAXRD) of TiO$_2$, synthesized silica and SO$_4{}^{2-}$/TiO$_2$ catalyst which supported by silica. Sample silica which was characterized shows an area of diffusion peak or amorph peak in accordance with Bragg corner recorded as around 2θ = 23.43° [8]. This data proves that this sample is amorph phase silica. Specifically for catalyst characterization, areas of diffusion peaks were recorded at 2θ = 25.19^0, 37.67^0, 47.90^0, 53.75^0 and 54.92^0. This peak indication supports the existence of active sites SO$_4{}^{2-}$/TiO$_2$ as noted in previous studies [3], [9], [10].
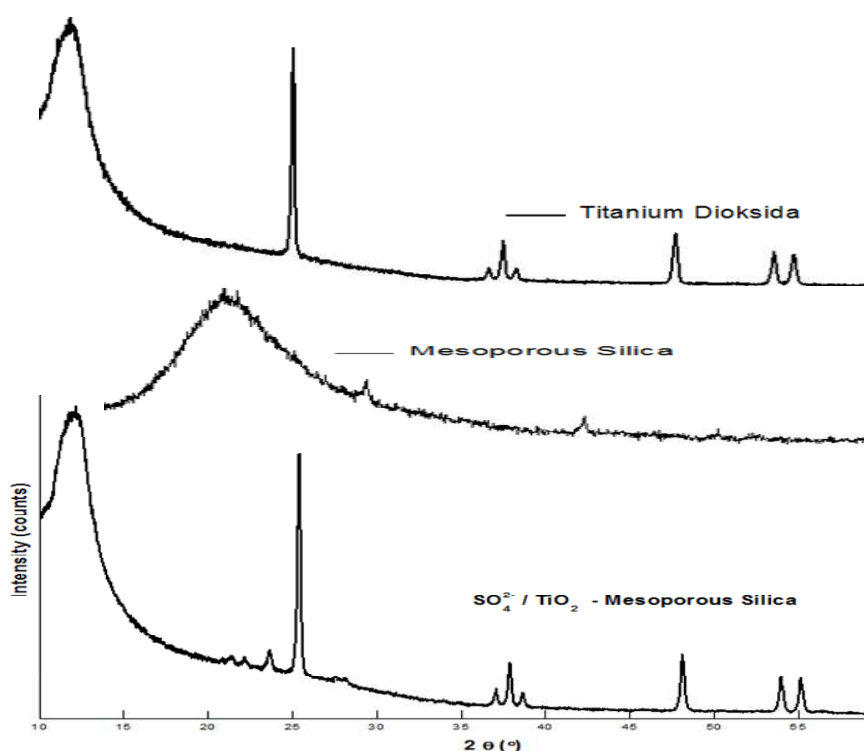
Figure 1. Diffractogram of TiO₂ , Mesoporous Silica, and Catalyst

In Figure 2 it is indicated 2 types of a curve between isotherm adsorption-desorption of silica and catalyst which had been synthesized. It seems that the hysteresis loop is related to isotherm adsorption of nitrogen on silica and catalyst surface
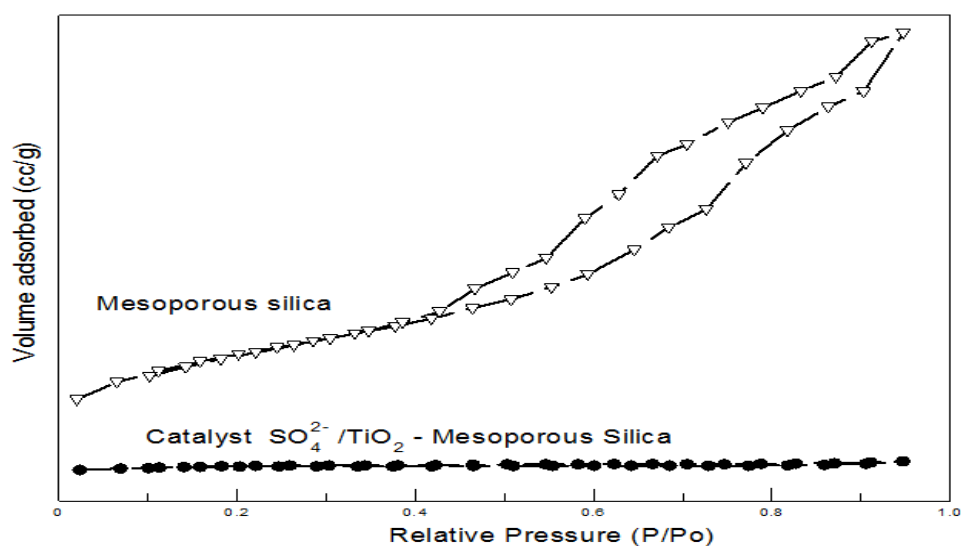

Figure 2. N₂ adsorption-desorption isotherm curve for silica and catalyst

First curve (catalyst) is isotherm type II is monolayer-multilayer adsorption. The second curve is classified as type IV (silica), in which curve only can be formed for mesoporous solid produced

through adsorption multilayer followed by capillary condensation. Silica characterization shows isotherm type IV by forming a hysteresis loop in accordance with type H1. This loop hysteresis indicates that this silica has uniform mesopore structure [8], [11]. Relatively wide loop hysteresis silica inform that there is adsorbate/gas adsorb and condensed in a pore and capillary system of the material [12].

Isotherm curve adsorption-desorption for catalyst supported by mesoporous silica shows isotherm type II and very narrow hysteresis loop area. This phenomenon indicates that this catalyst has no uniform array pore as mesopores [13].

Table 1. BET analysis of silica and catalyst

Catalyst	Total Pore Volume ($cm^3.g^{-1}$)	Average Pore Size (nm)
Silica	0.22381	3.2864
Catalyst (SO_4^{2-}/TiO_2 –Mesoporous Silica)	0.004699	1.6104

BET characterization was conducted to determine the volume and pore size of synthesized silica and catalyst. The result of pore characterization shows that pore size silica was 3.2864 nm and pore volume was 0.22381 $cm^3.g^{-1}$. This phenomenon proves that silica was categorized as mesopore with a pore size of 2 nm-50 nm (IUPAC). The results of the BET analysis of the catalyst in the data in Table 2 recorded smaller pore properties after silica was modified with SO_4^{2-}/TiO_2. Based on pore characteristics, it can be concluded that the silica sample is mesoporous and can be used as a support of SO_4^{2-}/TiO_2 [14].
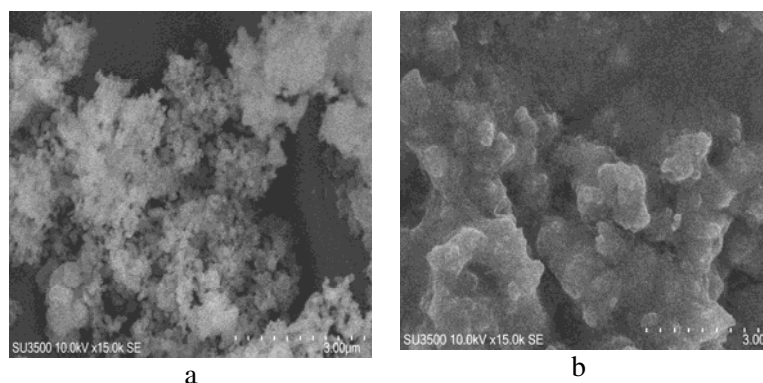

a   b

Figure 3. (a). Micrograph of mesoporous silica ; (b). Micrograph of catalyst

This Figure 3 shows the physical and microstructure change and difference of silica and catalyst. After silica the with active sites of SO_4^{2-}/TiO_2, the overlapping aggregate was formed due to the effect of high temperature in calcination. The existence of active sites of SO_4^{2-}/TiO_2 and silica have been merged through impregnation. This phenomenon shows that the preparation process of catalyst through impregnation followed by calcination was a success.

The microstructure of catalyst is seemed to be thickened so that pore size and volume is smaller as summarized in table 1. Besides the synthesis of catalyst material and its support, this study is also tried its application. This catalyst is designated for the esterification reaction of free fatty acid contained in palm fatty acid distillate (PFAD).

3.2   *Palm Fatty Acid Distillate Esterification*

In every variation of catalyst weight ratio used, unreacted fatty acid of the reaction product obtained is analyzed by acid-base titration for conversion calculation. The best reaction product which has the lowest fatty acid, it was then re-analyzed by using GC-MS so that it can be calculated of obtained ethyl ester.
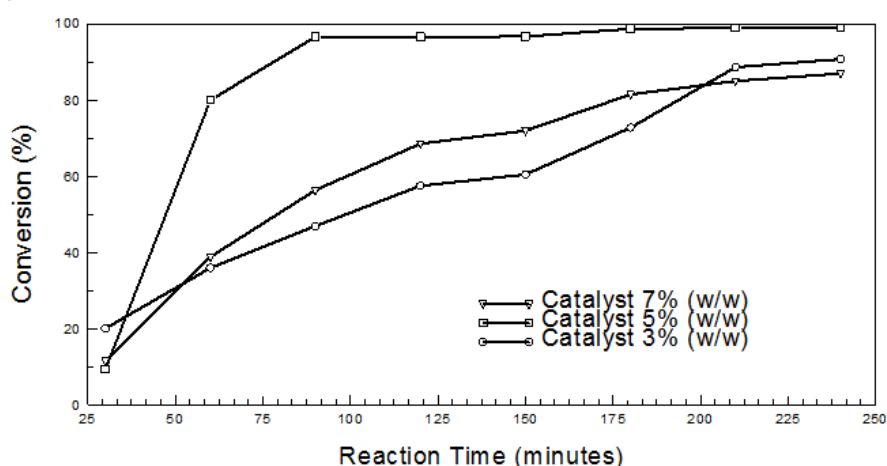

Figure 4. The relation between reaction time versus conversion at the variation of the catalyst amount.

Figure 4 shows the reaction process occurred in catalyst variation of 3%, 5%, and 7%. The observation and analysis of the sample were conducted started from 30 minutes up to 240 minutes and it was determined at 90 minutes for 5% catalyst as the best process. In which in this condition reaction occur rapidly with the conversion of ester-forming reaction had close to maximum conversion. Based on the result of the observation of 3 experiments of catalyst amount variation, it can be concluded that maximum conversion can be achieved at 98.9% at 210 minutes for 5% catalyst load. High conversion will facilitate separation of remaining fatty acid from ester as the main product.

Data on Table 2 shows that physical properties as biodiesel including viscosity at 40^0C and density at 15^0C the best reaction product which meets the requirement of ASTM D-6751-02] [15], [16], [17]. These physical properties give information that the esterification reaction path has successfully change fatty acid contained in PFAD into an ester.

Table 2. Viscosity and density of the reaction product

Parameters	Unit	Value	ASTM D-6751-02
Density at 15 ^{o}C	kg/cm³	871.3	870 – 900
Viscosity at 40 ^{o}C	mm/s²	4.6555	1.9 – 6.0

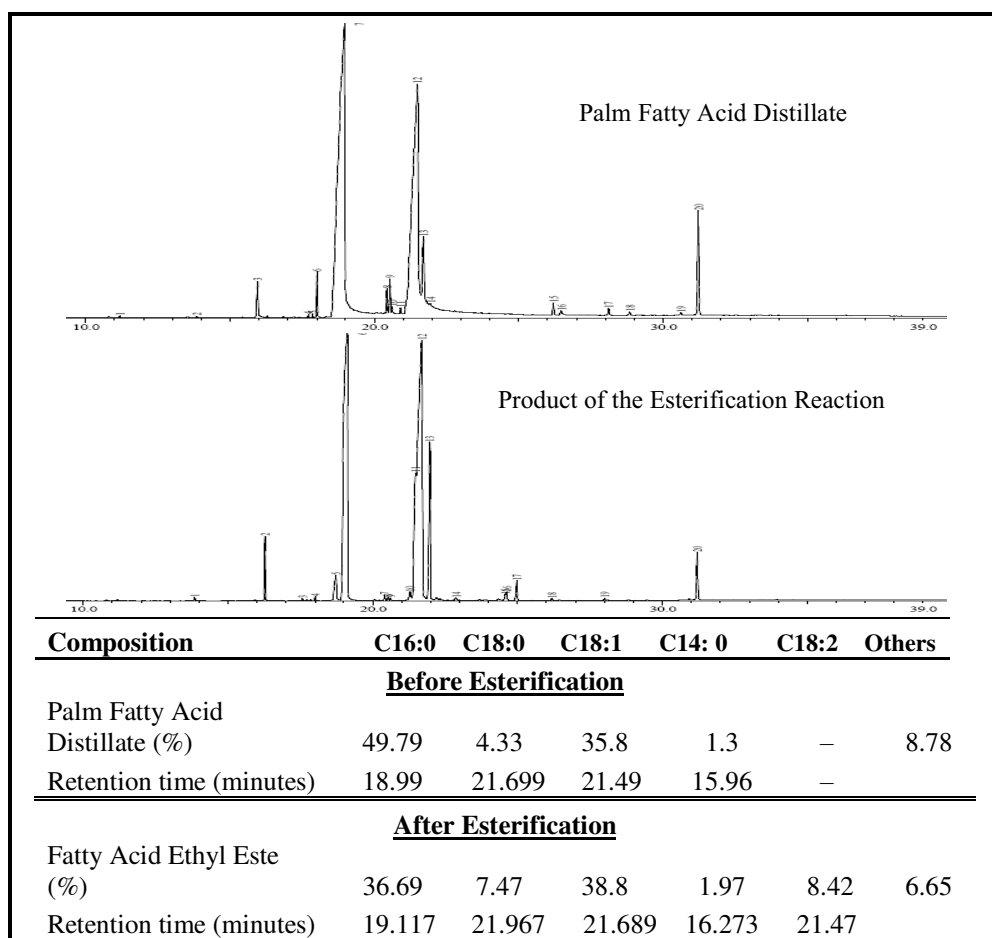| Composition	C16:0	C18:0	C18:1	C14: 0	C18:2	Others
Before Esterification						
Palm Fatty Acid Distillate (%)	49.79	4.33	35.8	1.3	–	8.78
Retention time (minutes)	18.99	21.699	21.49	15.96	–	
After Esterification						
Fatty Acid Ethyl Este (%)	36.69	7.47	38.8	1.97	8.42	6.65
Retention time (minutes)	19.117	21.967	21.689	16.273	21.47	

Figure 5. Chromatogram of PFAD and the product of esterification reaction

Identification through GC-MS analysis was conducted to obtained composition data of fatty acid component and ethyl ester. In this step, it was determined to observe 5 components which have an effect on the cetane number from biodiesel. As known that high cetane number shows the best quality of biodiesel. Figure 5 shows ethyl ester (C16:0, C18:0, and C18:1) as palmitate, stearate and oleic as 3 major components. Alkyl ester from three-component has cetane number around 55-58 (C18:1) up to more than 80 (C16:0 and C18:0) [18] from this data it can be concluded that synthesized catalyst has a performance for PFAD esterification into ethyl ester. PFAD components contained within can be feedstock to produce the best quality for the biodiesel ester shown in Figure 6.

palm fatty acid distillate

fatty acid ethyl ester (biodiesel)

Figure 6. Palm fatty acid distillate and fatty acid ethyl ester (biodiesel)

4   Conclusion

It was concluded that the synthesized silica has mesopore characteristics. This silica can be composited with the active site and serves as a support in catalyst preparation. The synthesized catalyst has a high performance in the esterification reaction from palm fatty acid distillates to ethyl fatty acid esters as biodiesel.

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