The Correlation of Biodiesel Physical Properties and Titanium Tetrahedral Coordination in Silica-Titania Prepared by Different Moles Ratio of Titania Precursors

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Abstract

Palm oil cannot be used directly as biofuel due to its high boiling point and viscosity. For its application as biofuel, the palm oil is converted to biodiesel through transesterification of palm oil and methanol with catalyst addition. This work is related to the synthesis of silica-titania as catalyst in association with titanium tetrahedral coordination and the study of the effect of titanium tetrahedral coordination on biodiesel production from palm oil. A solid state method is used to synthesize silica-titania catalyst applying mole variation of both solid silica and titania. The synthesis products are characterized by FTIR and DR UV-Vis, as well as the fraction of titanium tetrahedral coordination is calculated through deconvolution method of DR UV-Vis spectra. The results show the tetrahedral coordination of titanium increased using both solid silica and titania in the solid state method compared to that using solid titania commercial as precursor in the reaction. The mole ratio of silica and titania of 1:0.5 gave the highest percentage of titanium tetrahedral coordination. The increasing of the fraction of titanium tetrahedral coordination in silica-titania catalyst applied in reaction of palm oil and methanol can reduce the boiling point, viscosity, and density of the oil product.

Keywords: silica-titania, titanium tetrahedral coordination, biodiesel, palm oil, solid state

1. Introduction

Based on several reasons in relation to (i) limitation of fossil fuel natural resources, (ii) current cost of crude oil, and (iii) environmental pollution generated by fossil fuel usage, some research on biodiesel energy have been investigated during recent decades. Biodiesel has been considered as one of alternative fuel energy due its special advantage over common fossil fuel energy. Furthermore, biodiesel has several benefits related to (i) its better lubricating properties compared to that of fossil fuel, (ii) reducing too fast engine exhausted, and (iii) economic factor of engine maintenance (Gaurav, et al., 2016; Ilmi et al., 2017).

Indonesia is a country rich with palm oil and therefore, biodiesel can be produced from palm oil through some treatments. In addition, palm oil can live longer (about 25 years) and resist towards climate problem. According to Axelsson et al. (2012), the application of palm oil for biodiesel production is not reducing the availability of palm oil for consuming need.

It is known that a homogeneous catalyst is required in the reaction of vegetable oil with high free fatty acid content with short chain alcohols. Meanwhile a heterogeneous catalyst is suitable for tranesterification reaction of vegetable oil with low free fatty acid and short chain alcohols such as methanol and ethanol. The homogeneous catalysts such as sulfuric acid, hydrogen chloride, sodium hydroxide, and potassium hydroxide yielded a problem related to separation process of product and catalyst. As a result, a higher cost factor is needed for the more complex separation. In addition to the incomplete separation between biodiesel product and catalyst may generate problem related to engine corrosion (Talebian et al., 2013). The limitation of homogeneous catalyst can be solved by the application of heterogeneous catalyst since the phase of heterogeneous catalyst is different from the phase of biodiesel product. The separation process is more easy and low cost. Moreover, the heterogeneous catalyst is reusable for other reactions (Chouhan et al., 2011).

One of the famous heterogeneous and very versatile catalysts in the group of titano silicate is silica-titania (SiO_2-TiO_2). It is known that the role of titanium tetrahedral coordination is very important in catalytic activity of silica-titania. The formation of titanium tetrahedral coordination via Si-O-Ti bond yields acidity on silica-titania surface caused by different geometrical form and coordination between Si and Ti (Nizar, et.al, 2013). Up to date, the application of surface acidity which occurred as the present of titanium tetrahedral coordination in silica-titania catalyst for biodiesel production has not been reported yet. However, a literature study ever reported a substituted sulfate group of silica-titania as catalyst in biodiesel production. Generally, the catalytic activity of silica-titania and titania sulfate is stronger with 90% achievement of conversion. According to Shao et al. (2013), the increased percentage of biodiesel production is not directly proportional with the increased percentage of sulfate group in silica-titania .

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The mole ratio of Si and Ti believed as one of the factors affected the number of titanium tetrahedral coordination in which the mole of Ti must be small equal to Si mole. It was agreed when the mole ratio of titania higher than that of silica, the formation of Si-O-Ti had been blocked by Ti-O-Ti bonding. The presence of Ti-O-Ti bond indicates the formation of titanium in octahedral coordination that means the silica and titania precursors are not reacted. Therefore, the objectives this studies firstly, to investigate the effect of mole ratio of solid precursors to the formation of titanium tetrahedral coordination in silica-titania catalyst. Secondly is to study the effect of titanium tetrahedral coordination to the physical properties of biodiesel production yielded from transesterification reaction of palm oil and methanol.

2. Method

2.1. Materials

Analytical grade of titanium oxide (Acros), silica (Sigma Aldrich), and toluene (Merck) were used in this study for the synthesis of silica-titania catalyst. Palm oil (Bimoli) and methanol (Merck) were used for biodiesel production through transesterification reaction using the proposed silica-titania catalyst.

2.2. Synthesis of silica – titania by solid state method

The silica-titania catalyst is synthesized by reacting solid precursor of silica and titania in toluene using solid state method. In order to obtain the silica-titania catalyst with high percentage of titanium tetrahedral fraction, the mole ratio of titania should be the same or lower than that of silica, thus, the variation of mole ratio using titania of 1.0, 0.50 and 0.25 compared to 1.0 mole of silica. A mixture of silica and titania in toluene was sonicated using ultrasonic apparatus for 1h to obtain homogeneous mixture. Afterwards, the mixture was put in a fumehood for 24h to evaporate toluene. Next, the mixture was calcinated at 450^{o}C for 8h and then the mixture was kept in a dessicator for characterization and biodiesel synthesis (Ningsih, 2015; Nizar et al., 2013; Shao et al., 2013).

2.3. Characterization study of silica-titania catalyst

The FTIR examination was used to determine the chemical bonding in the mixture of silica and titania. The samples were detected in the range of 4000–400 nm^{-1}. The DR UV-Vis investigation was used to determine tetrahedral and octahedral coordination in the sample and also to calculate the fraction of titanium tetrahedral based on UV spectral deconvolution. The samples were analyzed in wavelength range of 200 – 400 nm.

2.4. Silica-titaniacatalyst for biodiesel production

The production of biodiesel was obtained by transesterification reaction of commercial palm oil and methanol in the existence of silica-titania catalyst. The mole ratio of methanol and palm oil was taken to be 6 : 1 and the quantity of catalyst was taken by 10% of the palm oil weight. All components were mixed using a magnetic stirrer and heated for 3h at 65^{o}C. Afterwards, the mixture was cooled followed by separation process of the product, catalyst and excess methanol (Lokman et al., 2016).

The first separation process was conducted to remove catalyst using centrifuging. The second separation process was conducted to remove excess methanol using rotary evaporator at temperature higher than the boiling point of methanol. The biodiesel product was examined by FTIR while the physical properties of biodiesel were determined for its boiling point, viscosity, and density. The prepared catalysts and biodiesel formed are summarized in Table 1.

Table 1. The prepared catalysts and biodiesel product

Sampel	Mole silica	Mole titania	Biodiesel product
TiO_2	-		Bio-T
ST (1-1)	1,00	1,00	Bio(1:1)
ST (1-0,5)	1,00	0,50	Bio(1:0,50)
ST (1-0,25)	1,00	0,25	Bio(1;0,25)

3. Results and Discussion

3.1. FTIR spectra of silica-titania series

Fig.1 shows FTIR spectra of TiO_2, SiO_2, and series of SiO_2-TiO_2 formed by syntheses at wave number range of 4000 – 600 cm^{-1}. Moreover, the main absorption bands of TiO_2 spectrum are detected at wave number 2352 cm^{-1} and 734 cm^{-1} respectively, which indicate vibrations of Ti-O (Ti-O-Ti). The main absorption band of SiO_2 spectrum at wave number of 1058 cm^{-1} indicates asymmetric vibration of Si-O-Si, while the main absorption band at wave number of 803 cm^{-1} indicates symmetric vibration of Si-O-Si (Shao et al., 2013).

The FTIR spectra of SiO_2-TiO_2 show main absorption bands at respected wave numbers of 3668 cm^{-1}, 3429 cm^{-1}, 960 cm^{-1}, and 749.42 cm^{-1}. In general, the FTIR spectra of SiO_2-TiO_2 series are similar and appear as combination spectra of SiO_2 and TiO_2. The absorption bands at wave number of 3668 cm^{-1} and 3429 cm^{-1} indicate stretching vibrations of -OH from silanol group (Si-OH) or water vapor adsorbed on material surface. The absorption band of –OH detected in the synthesized samples are due to samples which exposed in open air during sample measurement by FTIR. The absorption band at wave number of 749.42 cm^{-1} is suggested the absorption band of Ti-O-Ti. A very weak intensity of vibration band is observed at wave number of 960 cm^{-1}, this absorption band indicates a vibration of Si-O-Ti bonding.The Si-O-Ti bonding was formed due to chemical interaction between SiO_2 and TiO_2 and this bonding is a sign of tetrahedral framework formation in the synthesis of SiO_2-TiO_2 (Kim, et al., 2000; Nizar et al., 2013).

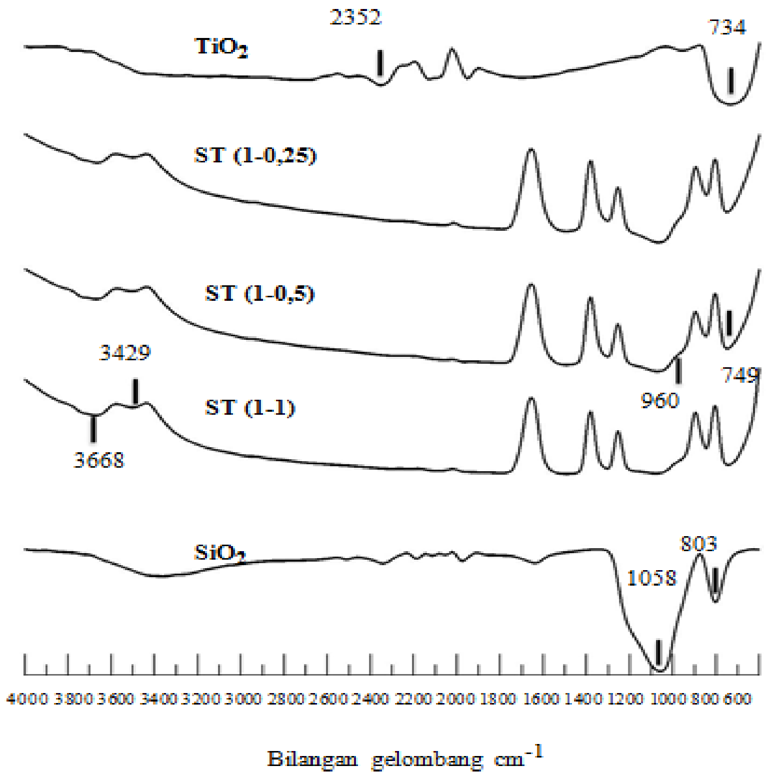
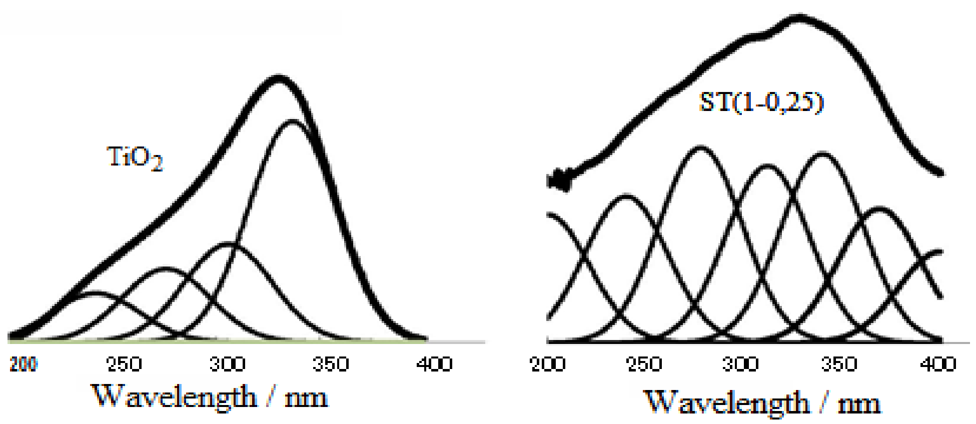


Fig.1. FTIR spectra of respected TiO_2, SiO_2, and SiO_2-TiO_2 series

The absorption band at wave number of 960 cm^{-1} is an expected absorption band because this absorption band is an indicate on of tetrahedral framework formation with the existence of Si-O-Ti bonding (Chen, et al., 2012; Kim, et al., 2000; Nizar et al., 2013). The existence of tetrahedral framework in the synthesis of silica-titania shown by FTIR spectra is more confirmed by justification of absorption band shown by DR UV-Vis examination.

3.2. Deconvolution spectra of DR UV-Vis of silika-titania series

Fig. 2 shows diffuse reflectance spectra of UV-Vis of SiO_2-TiO_2 series and TiO_2. Deconvolution on spectra was examined to investigate the effect of mole ratio of SiO_2 and TiO_2 precursors on tetrahedral framework and to determine the quantity of tetrahedral fraction formed by Si-O-Ti bonding. A literature study reported that at wave length range of 200 - ≤ 270 nm of DR UV-Vis spectra is an absorption range of titanium tetrahedral, while titanium octahedral coordination is observed at wavelength range of ≥270 – 400 nm ((Nizar et al., 2013; Sosnov, et al., 2010).



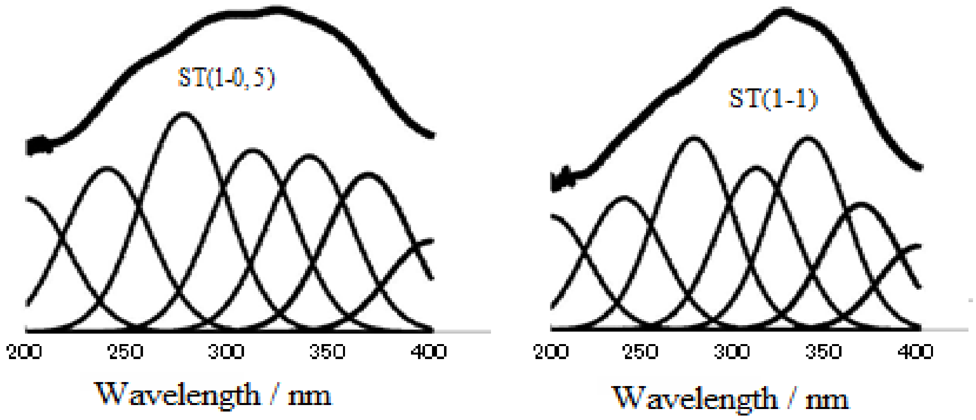


Fig. 2. Deconvolution spectra of DR UV-Vis of SiO_2-TiO_2 series and TiO_2

In general, the SiO_2-TiO_2 catalyst formed on the basis of mole ratios of SiO_2:TiO_2 may have dominant octahedral fraction, however, the catalyst synthesized under this study showed an increase of tetrahedral fraction. The increasing of tetrahedral fraction yielded can be read from Table 2.

Tabel 2. The percentage of titanium tetrahedral fraction on the basis of deconvolution of DR UV-Vis spectra

Sample	Titanium tetrahedral fraction
TiO_2	33, 40
ST(1-0,25)	42,84
ST(1-0,5)	44,70
ST(1:1)	42,05

Based on the results shown at Table 2, the solid state reaction of silica and titania at 450°C can increase the quantity of titanium tetrahedral fraction from 33% to almost 50%. The spectra deconvolution justified a large part of TiO_2 and SiO_2 formed Si-O-Ti bonding. More Si-O-Ti bonding can be formed when the quantity of TiO_2 is lower than that of SiO_2. When the quantity of TiO_2 is higher than that of SiO_2, the titanium octahedral fraction is likely being formed through Ti-O-Ti bonding. However, there is no standard based on the ratio of Si : Ti in the synthesis of silica-titania (Ren, et al., 2008). The results shown by spectral deconvolution of DR UV-Vis is in good agreement with that of FTIR spectra by the appearance of absorption band at wave number of 960 cm^{-1}.

3.3. Application of silica-titania catalyst in biodiesel production

In general, the reaction between palm oil and methanol using a catalyst may produce biodiesel (methyl ester with gliserol as side product) or soap (Alhassan, et al., 2015; Konwar et al., 2015; Lokman et al., 2016). The product may have solid phase if soap is formed. However, the reaction between palm oil and methanol using SiO_2-TiO_2 or TiO_2 have yield a product with liquid phase which indicated the production of biodiesel. The biodiesel product separated by using a centrifuge and rotary evaporator. In order to confirm that palm oil is converted into biodiesel, an examination of physical properties (density, viscosity, and boiling point) on biodiesel product is required. The difference of physical properties between palm oil and the product indicates that palm oil has already converted to biodiesel.Table 3. shows the physical properties of palm oil and biodiesel at room temperature.

Table 3. Physical properties of palm oil and biodiesel at room temperature.

Physical properties	Palm oil (Bimoli)	Biodiesel			Unit
		Bio (1:1)	Bio(1:0,5)	Bio(1:0,25)	
Density	0.905	0.898	0.897	0.899	g/ml
Viscosity	0.090	0.100	0.100	0.100	ml/s
Boiling point	315	290	270	294	°C

Data from Table 2 and Table 3 with respect to titanium tetrahedral fraction can be used to examine the effect of quantity of titanium tetrahedral fraction on physical properties of biodiesel with respect to its boiling point, viscosity, and density. Fig. 3(a) and 3(c) shows increased titanium tetrahedral fraction resulting a decrease in both boiling point and density of biodiesel, respectively. Fig. 3(b) shows increased titanium tetrahedral fraction yielded indifferent values of viscosity of biodiesel. However, based on data in Table 3 with respect to the viscosities of palm oil and biodiesel, the existence of titanium tetrahedral fraction in silica-titania catalyst may change the value of their viscosities.

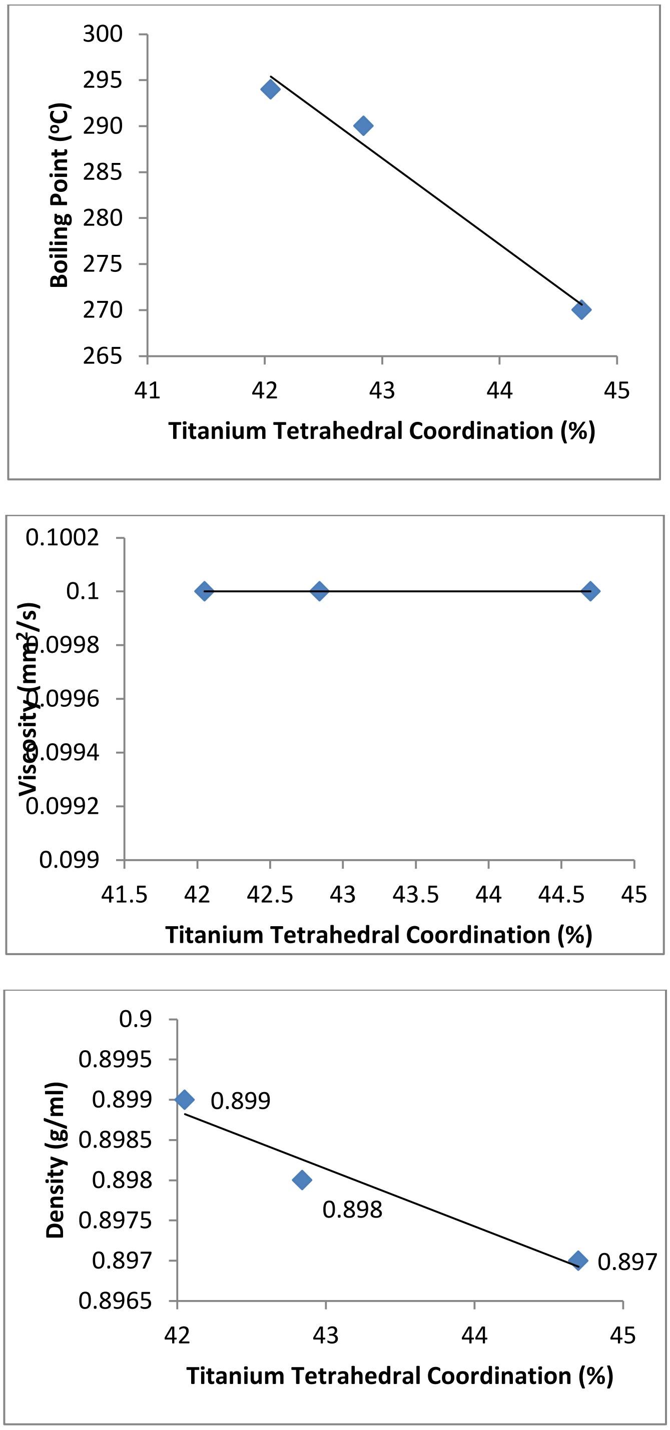


Fig.3. Effect of titanium tetrahedral fraction on physical properties of synthesized biodiesel with respect to boiling point, viscosity, and density.

4. Conclusion

The series of silica-titania catalyst, which is formed through solid state method using solid silica and titania as precursors, is very substantial for transesterification reaction in biodiesel production. This study shows the existence of titanium tetrahedral fraction may improve the physical properties of synthesized biodiesel.

Acknowledgement

We gratefully acknowledge the funding from **Kementerian Riset dan Teknologi Indonesia** and **Universitas Negeri Padang** for financial support under PNPB 2017 research grant.

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