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Original Research Article

Catalytic Activity of Reused SiO_2-TiO_2 on Biodiesel Production from Waste Cooking Oil in Various of Catalyst Loading

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ABSTRACT

The reusability of silica-titania catalyst on biodiesel production from waste cooking oil in various of catalyst loading has been investigated. The reused silica-titania catalyst has been obtained by washing the previous catalyst used in biodiesel production from palm and waste cooking oils based on various of catalysts loading. The DR UV-Vis has been used for characterization of reused silica-titania catalyst to investigate the existence of titanium tetrahedral coordination in that given catalyst. In order to get information about the catalytic activity of reused silica-titania catalyst, several analyses were carried out on biodiesel products such as density, flow rate and acid number, as well as FTIR for characterization. The results show that the fraction of titanium tetrahedral coordination decreased after silica-titania catalyst reused in reaction of transesterification between waste cooking oil and methanol. The decrease of titanium tetrahedral fraction in reused silica-titania catalyst yields a reduction in its catalytic activity in biodiesel production. The density, flow rate, and acid number analyses show the 7% of catalyst loading was the optimum condition for biodiesel production from palm and waste cooking oils using reused silica-titania catalyst. The FTIR spectra of biodiesel products are almost similar to that of waste cooking oil, however, there is dissimilarity on band area in the wave number range of 1250–1000 cm^{-1} attributed to vibration of C–O–C or C–O–H.

Keywords: Reused, catalyst loading, Biodiesel, Silica-titania catalyst, Waste cooking oil, Flow rate, Density, Acid number.

INTRODUCTION

Fast population growth rate and industrial process have yielded higher energy consumption. On other side, the available unrenewable energy sources like petroleum oil, coal, and natural gas are reduced. [1] Therefore, alternative renewable energy sources are still seeking and biodiesel meets the requirement. Biodiesel as one of alternative renewable energy sources can be produced from vegetable oils, animal lard, and waste cooking or fying oil. [2] Biodiesel has superiority over safety, non toxic, biodegradable, sulfur free, less CO releasing, high flash point, and friendly environmental. [3-5] Besides, biodiesel reduces green house effect compared to diesel from petrol oil. Significant biodiesel utilization can reduce CO (≈ 44%) and SO_2 (100%). [6]

Several sources like vegetable oils and animal lard can be used to yield biodiesel such as oils from sunflower, soybean, coconut, zaitun, and hazelnut, as well as chicken lard and fish oil by-product and waste frying oil. [7,8] Palm oil is more promising since Indonesia is the biggest country in the world yielding palm oil. [9]

Waste cooking or frying oil is promising feedstock for biodiesel production, because this oil is more economic and easily available in many places such as household, hotels, and food industries. The choice of waste cooking oil for biodiesel production can overcome environmental pollution due to high content of FFA (Free Fatty Acids) in this type of oil. The oil waste can also reduce land for palm plantation. [6]

Biodiesel can be produced through transesterification reaction between vegetable oil and short chain alcohol. [10,11] This reaction is to reduce viscosity of vegetable oil or lard by forming an alkyl ester. The transesterification reaction is a slow reaction and therefore, a catalyst is needed for this reaction. [2] Previous report stated that this research group conducted biodiesel production using silica-titania catalyst synthesized by solid state method, with respect to titanium tetrahedral framework. [12] The synthesis of silica-titania catalyst used solid state method. This previous work emphasized on titanium tetrahedral effect on properties of biodiesel product. The results showed that titanium tetrahedral fraction gave effect on properties of biodiesel like boiling point, viscosity, density, and acid number.

Previous investigation also reported that this research group had studied the effect of silica-titania catalyst loading on biodiesel production from palm and waste cooking oils. The conversion of palm oil to biodiesel was found to be 33.33% using optimum mass of silica-titania catalyst as 7%, while the conversion of waste cooking oil to biodiesel obtained was found to be 91.25%. This phenomenon indicated that silica titania as acid catalyst is effective and appropriate for vegetable oil with high content of FFA such as waste cooking oil. [13]

On account of those reasons stated above, up to date, the optimization of catalyst loading applying reused silica-titania catalyst for biodiesel production from waste cooking oil has not been reported yet. Therefore, the present work has investigated the catalytic activity of reused silica-titania catalyst for biodiesel production from waste cooking oil in various of catalyst loading.

MATERIALS & METHODS

Materials and Equipments

The materials in this study were used for catalyst preparation and biodiesel production. The reused silica-titania catalyst was obtained by washing the catalyst that had already used in previous reaction. The given catalyst was washed by hexane and methanol. The biodiesel production needed waste cooking oil, methanol, KOH, and pp indicator.

The equipments used in this study included equipment for examinations and characterization. For synthesis of biodiesel, this study needed glassware, hot plate stirrer, oven, balance, thermometer, stirrer, centrifuge, ultrasonic, and rotary evaporator. The instrument used for characterization of silica-titania catalyst was the DR UV-Vis spectrometer while the FTIR spectrometer was used to characterized biodiesel products.

Methods

Preparation of reused SiO_2-TiO_2 catalyst

The silica-titania catalyst previously used in biodiesel production from palm and waste cooking oils was washed by n-hexane to remove all non polar components and followed washing by methanol to remove all polar substituents attached to the given catalyst and then the catalyst was dried in an oven at 105^oC for 2h and stored in a desiccant before reused it. [14,15] The second reused was conducted applying the same procedure as above.

Characterization of reused SiO_2-TiO_2 catalyst

The reused catalyst before transesterification reaction was characterized by DR UV-Vis in the wavelength range of 200-400 nm. The spectra obtained were then deconvoluted using Gaussian function to calculate the

number of titanium tetrahedral coordination in the reused silica-titania catalyst. [16]

Application of reused silica-titania catalyst

The catalytic activity of reused silica-titania catalyst biodiesel production was investigated. The biodiesel production was done through transesterification reaction between waste cooking oil and methanol in the presence of reused silica-titania catalyst. The reaction was done in a three bottle-neck Erlenmeyer (250 mL) in a reflux system at 65^{o}C for 5h using a mol ratio of 6:1 between methanol and waste cooking oil. [16] The catalyst loading of reused catalyst to waste cooking oil were set at 1%, 3%, 5%, 7%, and 9%. [13] After setting the reaction time, the reaction product was the cooled and followed by separation of catalyst and excess methanol from the product. The reused silica-titania catalyst was separated by centrifuge while the excess methanol in product was removed applying a rotary evaporator at temperature above the boiling point of methanol. The same procedure was conducted for application of the 2nd reused silica-titania catalyst.

FTIR characterization and examination of biodiesel properties.

In order to get information of the catalytic activity of reused silica-titania, the biodiesel product from waste cooking oil was characterized by FTIR. In addition, several properties were also tested such as density, flow rate, and acid number. Then the results of properties examination were compared to that of waste cooking oil. All biodiesel products were summarized in Table 1

Tabel 1. Labeling biodiesel products

1st reusability			*2nd reusability*		
No	Catalyst loading (%)	Biodiesel label	No	Catalyst loading(%)	Biodiesel label
1	1	BCR1-1	1	1	BCR2-1
2	3	BCR1-3	2	3	BCR2-3
3	5	BCR1-5	3	5	BCR2-5
4	7	BCR1-7	4	7	BCR2-7
5	9	BCR1-9	5	9	BCR2-9

Note :
BCR1 :*Biodiesel of 1st catalyst reusability*
BCR2 :*Biodiesel of 2st catalyst reusability*

RESULT AND DISCUSSION

DR UV-Vis spectra of silica-titania catalyst (1st*reusability and 2ndreusability)*

Properties of physico-chemica of reused silica-titania catalyst were characterized by DR UV-Vis to determine the fraction of titanium tetrahedral coordination formed through S-O-Ti bonding. The DR UV-Vis spectra in wavelength range of 200–285 nm are attributed to titanium tetrahedral fraction, while at wavelength above 285 nm attributed to titanium octahedral fraction. [16]

The DR UV-Vis spectra of reused silica-titania catalyst show that the fraction of titanium tetrahedral coordination is lower than that of previously given silica-titania. The respective absorption bands at 230, 255, and 285 nm in deconvolution area of DR UV-Vis spectra are attributed to titanium tetrahedral fraction while absorption bands at 315, 345, and 360 nm are attributed to titanium octahedral fraction. Furthermore, the deconvolution of DR UV-Vis spectra shows the fraction of titanium in tetrahedral coordination of reused silica-titania (1st) and reused silica-titania (2nd) are found to be 24.6% and 23.2%, respectively. This finding shows a decreasing of the fraction of titanium tetrahedral coordination compared to that of freshly prepared silica-titania catalyst (31.04%) applied in previous work. [13] The reduction of titanium tetrahedral fraction is due to effects of temperature and reaction time on stability of Si-O-Ti bonding. The stability of Si-O-Ti bonding may affect catalytic action of silica-titania resulting reduction of conversion to biodiesel production. However, the fraction of titanium tetrahedral coordination in reused silica-titania is still higher than that

of titanium tetrahedral coordination in commercial TiO_2 (23%). [17]

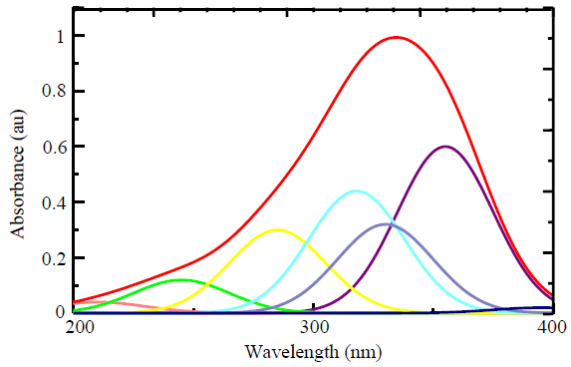

Fig.1. Deconvolution of DR UV-Vis spectra of reused SiO_2-TiO_2 (1st)

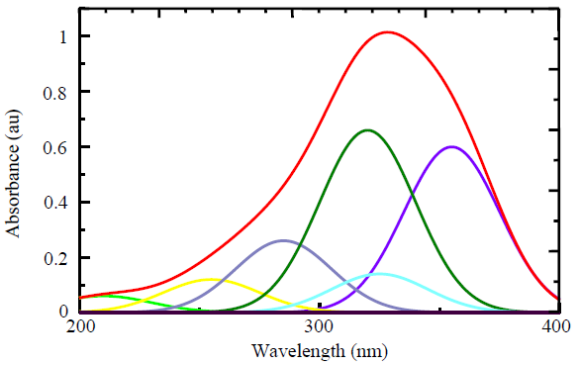

Fig.2. Deconvolution of DR UV-Vis spectra of reused SiO_2-TiO_2 (2nd)

Properties of biodiesel applied reused silica-titania catalyst

Viscosity

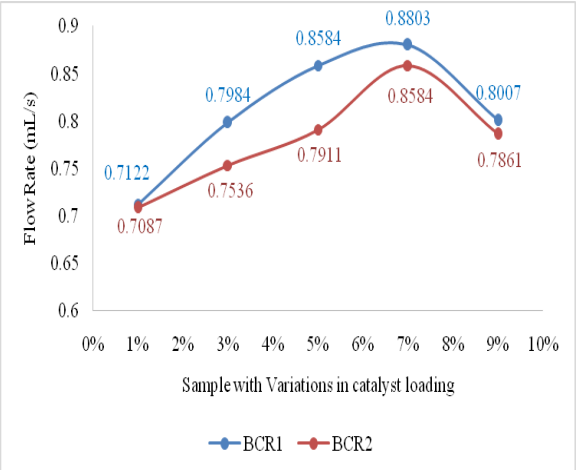

Fig. 3.Flow rate of biodiesel products based variation of catalyst loading

The flow rate examination is to assay viscosity of biodiesel product. Higher flow rate of biodiesel product yields lower viscosity, and vice versa. The results of flow rate of biodiesel products applied 1st reused and 2nd reused silica-titania catalyst are shown in Fig.3.

On the basis of mass variation on reused silica-titania catalyst the flow rate data obtained as follows: 1% (1.0630 mL/s), 3% (0.9746 mL/s), 5% (0.9680 mL/s), 7% (1.1764 mL/s), 9% (1.0203 mL/s). [13] The fow rate of waste cooking oil is shown as 0.7042 mL/s. Generally, the flow rates of biodiesel products applying reused silica-titania catalyst are increased compared to that of waste cooking oil. However, these flow rate data are lower than that obtained from previous work. [13] Fig.3 shows increased flow rates of BCR1 proportional with increased catalyst loading until 7% illustrated as follows: 0.7122 mL/s, 0.7943 mL/s, 0.8584 mL/s, 0.8803 mL/s. Then, the flow rate decreased to 0.8007 mL/s at reused catalyst addition of 9%.

Fig. 3 also shows flow rates of BCR2 that are elevated with elevated addition of reused catalyst (2nd) until 7% that is iilustrated as follows: 0.7087 mL/s, 0.7536 mL/s, 0.7911 mL/s, 0.8584 mL/s. Then the flow rate reduced to 0.7861 mL/s after addition of reused catalyst (2nd) of 9%.

Several factors affect the reduction of flow rate after optimum condition achieved. The first factor is related to formation of salt of fatty acid (soap) from FFA and TiO_2 found not formed as the silica-titania. The second factor is corresponding with increased viscosity retarded diffusion between reactant and catalyst yielding lower ester production. The third factor is concerned with excess catalyst loading impeding biodiesel production due to absorption on catalyst surface. [13]

Density

Densities of biodiesel products from waste cooking oil were measured by a picnometer and the results are shown in Fig. 4. With regard to densities of BCR1 that the density values decreased compared to that of waste cooking oil (0.877 g/mL). The

reduction of BCR1 densities is consistent with increasing catalyst loading until 7% and obtained as follows: 0.8204 g/mL, 0.8198 g/mL, 0.8178 g/mL, 0.8170 g/mL. Then the density increased again after catalyst addition of 9%, that was found to be 0.8201 g/mL. Similar pattern was also found for densities of BCR2 that their densities reduced compared to that of waste cooking oil and the reduction is consistent with increased catalyst loading until 7%, and illustrated as follows: 0.8237 g/mL, 0.8222 g/mL, 0.8196 g/mL, 0.8178 g/mL. Then density elevated again after addition of catalyst loading of 9%, i.e. 0.8221 g/mL.

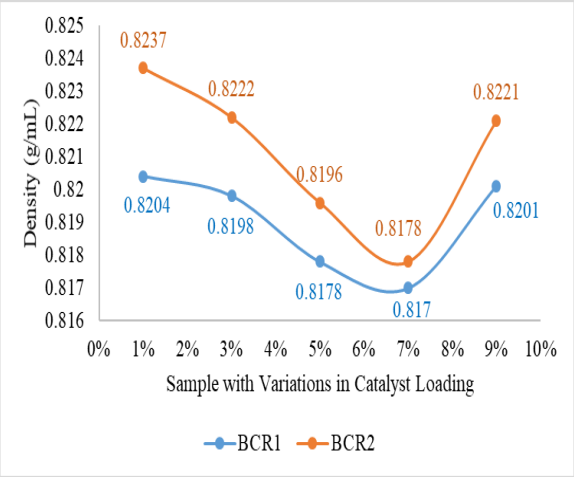

Fig. 4. Densities of biodiesel product based on variation of catalyst loading

Excess of catalyst causes slower diffusion between catalyst and reactant resulting elevated density of biodiesel product. Besides, the biodiesel product can be adsorbed on catalyst surface yielding lower methyl ester (biodiesel) product if excees catalyst loading applied. [18]

The results of density measurement are consistent with that of viscosity measurement of both BCR1 and BCR2 that increased flow rates consistent with decreased both viscosities and densities.

Acid number and percentage of conversion

The assignment of acid number is to determine the content of FFA in biodiesel products and the data of acid number of biodiesel based on variation of catalyst loading are illustrated in Fig. 5

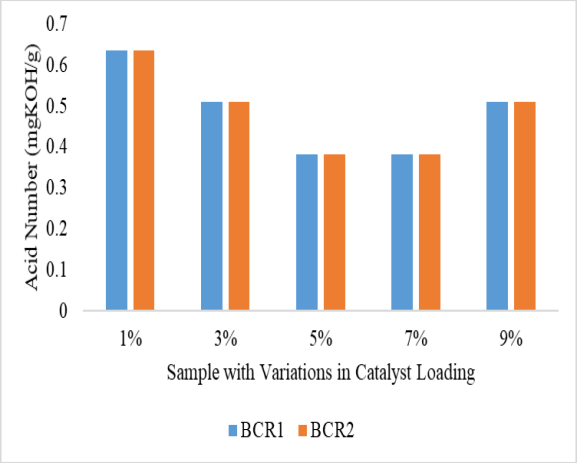

Fig. 5.Acid number of biodiesel products based on variation of catalyst loading

The results of acid number values of BCR1 are as same as that of BCR2 (Fig. 5) and found to be lower than that of waste cooking oil (1.87 mg KOH/g). The respective values of acid number of both BCR1 and BCR2 for catalyst addition of 1%, 3%, 5%, 7%, and 9% are as follows: 0.6358 mg KOH/g, 0.5086 mg KOH/g, 0.3815 mg KOH/g, 0.3815 mg KOH/g, and 0.5086 mg KOH/g. The data of acid number of biodiesel products, the percentage of both FFA and conversion of waste cooking oil to biodiesel products are illustrated in Table 2 for BCR1. Since the data for BCR2 are at same values as that of BCR1 with respect to acid number, %FFA, and % conversion, thus, the table data for BCR2 are the same as that for BCR1. It is peculiar that the data result for BCR1 and BCR2 in that occasion are same, it probably related to saponification process that is still unclear, however, there are differences in data for either BCR1 or BCR2 with regard to flow rate and density.

Tabel 2. % FFA and % conversion of BCR1 and BCR2 from waste cooking oil

Sample	Acid Number (mgKOH/g)	% FFA	% Conversion
Waste Cooking Oil	1.87	0.9350	
BCR1-1%	0.6358	0.3179	66 %
BCR1-3%	0.5086	0.2543	72.8 %
BCR1-5%	0.3815	0.1907	79.6 %
BCR1-7%	0.3815	0.1907	79.6 %
BCR1-9%	0.5086	0.2543	72.8 %

Table 2 show that %FFA of both BCR1 and BCR2 are lower than that of waste cooking oil; this is because that the FFA in waste cooking oil converted to FAME (Fatty Acid Methyl Ester) or biodiesel. The lowest %FFA of both BCR1 and BCR2 from waste cooking oil is found to be 0.1907 that is attributed to reused catalyst addition of 5% and 7%, respectively. On the other hand, the highest %FFA of both BCR1 and BCR2 is found to be 0.3197 that is corresponding with reused catalyst addition of 1%.

Value % FFA affects percentage of conversion of waste cooking oil to BCR1 and BCR2. The highest % conversion of waste cooking oil to BCR1 and BCR2 are found to be 79.6% at reused catalyst addition of 5% and 7%, respectively. On the other hand, the lowest % conversion of waste cooking oil to BCR1 and BCR2 are found to be 66% at reused catalyst addition of 1%.

From data of biodiesel properties (BCR1 and BCR2), it can be deduced that the silica-titania catalyst can be used repeatably as shown from its data of flow rate elevation and density reduction, as well as acid number of biodiesel products compared to that of waste cooking oil. The optimum reused catalyst loading for production of both BCR1 and BCR2 obtained by this study were taken as to be 7% with regard to the highest flow rate and lowest density presented by BCR1 and BCR2.

FTIR characterization of biodiesel products

FTIR characterizations of biodiesel products (BCR1 and BCR2) and waste cooking oil are illustrated in Fig. 6. The FTIR characterization is used to study the functional groups on its respective spectra.

Fig. 6 shows the FTIR spectra of waste cooking oil and both BCR1 and BCR2 applying optimum reused silica-titania catalyst loading (7%). There are main absorption peaks attributed to waste cooking oil illustrated at respective wavenumber of 2922.20 cm^{-1}, 2857.17 cm^{-1}, 1742.91 cm^{-1}, 1454.19 cm^{-1}, and 1159.51 cm^{-1}.The main absorption peaks of BCR1 are illustrated at respective wavenumber of 2922.54 cm^{-1}, 2857.52 cm^{-1}, 1742.66 cm^{-1}, 1453.24 cm^{-1} and 1160.54 cm^{-1}, while for BCR2 illustrated at 2922.28 cm^{-1}, 2857.48 cm^{-1}, 1743.20 cm^{-1}, 1454.05 cm^{-1}, and 1160.01 cm^{-1}.

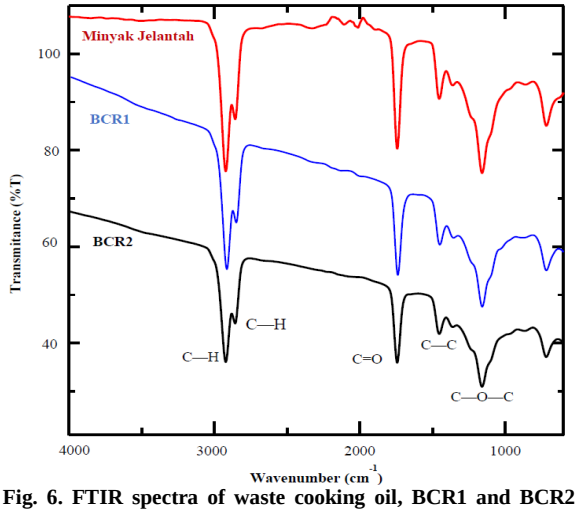

Fig. 6. FTIR spectra of waste cooking oil, BCR1 and BCR2 applying optimum reused catalyst loading (7%).

Absorption peaks at wavenumber range of 1250-1000 cm^{-1} attributed to C-O-C of methyl ester group, and weak absortion peaks appeared at wavenumber range of 1600-1450 cm^{-1} attributed to C-C bond. Strong absorption peak at wavenumber range of 3000-2800 cm^{-1}shows vibration of C-H of methyl group. [16] The significant difference of the two FTIR spectra is the change of ester group of waste cooking oil to methyl ester group of biodiesel product, [19] which is assigned by different of peak area in the range of 1250–1000 cm^{-1}. The absorption peak of waste cooking oil is more remarkable compared to that of BCR, while the absorption peak of BCR is wider and a shift of absorption peak at wave number from 1159.51 cm^{-1} to 1160.02 cm^{-1} occurred.

CONCLUSION

The conclusion of this study is that silica-titania can be reused. The fraction of titanium tetrahedral coordination in silica-titania catalyst decreased after reused in biodiesel production and catalytic activities

depend on the fraction of titanium tetrahedral coordination and catalyst loading. The optimum reused catalyst loading for both productions of BCR1 and BCR2 from waste cooking oil was found to be 7%. Respective properties of BCR1 with regard to flow rate, density, and acid number at optimum reused catalyst addition (7%) are found to be 0.8803 mL/s, 0.8170 g/mL, and 0.3815 mgKOH/g, and for BCR2 are found to be 0.8584 mL/s, 0.8178 g/mL, and 0.3815 mgKOH/g.

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