

# Reusability test of Silica-Titania Catalyst on Biodiesel Production from Waste Cooking Oil in Various Temperatures

Fiona Rachma Annisa<sup>1</sup>, Indang Dewata<sup>1</sup>, Hary Sanjaya<sup>1</sup>, Latisma Dj<sup>1</sup>, Ananda Putra<sup>1</sup>, Rita Sundari<sup>2</sup>,

Umar Kalmar Nizar<sup>1\*</sup>

<sup>1</sup>Chemistry Department, Universitas Negeri Padang, Jl. Prof Hamka, Air Tawar, Padang, West Sumatra, Indonesia

<sup>2</sup>Mechanical Engineering Department, Universitas Mercu Buana, Jakarta, Indonesia

\*Email : [umarjati77@gmail.com](mailto:umarjati77@gmail.com)

## ABSTRACT

This work has investigated the reusability of silica-titania in various temperatures (50 – 70°C) of biodiesel production from waste cooking oil. The reused silica-titania catalyst collected from silica-titania catalyst waste produced from the process of separating the catalyst from biodiesel products from palm oil and used cooking oil at various temperatures. The 1<sup>st</sup> and 2<sup>nd</sup> reused SiO<sub>2</sub>-TiO<sub>2</sub> were characterized by DR UV-Vis and the spectra were deconvoluted for calculate the fraction of titanium in tetrahedral coordination. In addition the biodiesel products were characterized using FTIR, and several properties of biodiesel such as density, flow rate and acid value were analyzed in order to get the information about catalytic activity reused SiO<sub>2</sub>-TiO<sub>2</sub>. The results show the titanium tetrahedral fraction in reused catalyst (1<sup>st</sup>) and (2<sup>nd</sup>) are found to be 24,98% and 24.65%, respectively. The FTIR characterization of biodiesel products and waste cooking oil are almost similar. The analysis of waste cooking oil converted to biodiesel shows an optimum temperature of 50°C that at this temperature the lowest density or highest flow rate gave highest conversion of 47.82% using BCR1 and 39.13% using BCR2.

**Keywords :** Biodiesel, Temperature, Reused Silica-Titania Catalyst, Properties of Biodiesel.

## I. INTRODUCTION

The availability of diesel oil from fossil fuel has become limited generated serious problem in fuel need nowadays. High consumption of fossil fuel and limited availability in nature, as well as non renewable energy sources has caused world oil price continually increased [1]. On account of this, biodiesel as alternative fuel produced from vegetable oil can be applied to replace diesel from fossil fuel [2], [3]

Waste cooking oil as one of vegetable oils is very potential as raw material for biodiesel production. The utilization of waste cooking oil for biodiesel production has saved waste discharge cost and maintenance. The free fatty acids (FFA) content in waste cooking oil can reduce environment quality around waste discharge. Therefore, waste cooking oil is a good choice as raw material to yield biodiesel [4]

The biodiesel can be produced through transesterification reaction between triglycerides of vegetable oil and short chain alcohol using a given catalyst. Methanol as a short chain of alcohol member can be applied for biodiesel production due to its low molecular weight and stable compared to other member of alcohol [5]

The usage of a catalyst is substantial because transesterification reaction is a slow reaction. There are three groups of catalysts that is commonly used in transesterification reaction, i.e acid, base, and enzyme catalysts. The acid and base catalysts are grouped into homogeneous and heterogeneous catalysts.

The application of homogeneous catalyst for biodiesel production has several disadvantages such as soap formation as a by-product, less stable, tedious separation process of the product resulting less biodiesel production. In order to overcome the drawback a heterogeneous catalyst is preferred to overcome problems faced by homogeneous catalyst [6], [7].

Silica-titania ( $\text{SiO}_2\text{-TiO}_2$ ) as one of heterogeneous catalysts possesses large application in academic and industrial field. Several silica-titania catalysts are used for photocatalyst, catalyst, sensor materials, and others. The silica-titania catalyst has large active area, thermally stable, transparent, and can be used to overcome the weakness of titania catalyst [8], [9].

This research group has already conducted optimization of reaction temperature using silica-titania catalyst in biodiesel production from palm and waste cooking oils. The highest percentage of conversion achieved 33.33% using palm oil at 65°C and 57.1% using waste cooking oil at 55°C. Based on data mentioned above silica-titania catalyst with its

acid properties is effective for reaction of waste cooking oil with high content of FFA [10]

This work has emphasized on the variation of temperature in biodiesel production from waste cooking oil applied re-used silica-titania catalyst by examinations on percentage of FFA and conversion, as well as properties of biodiesel products. This study has used silica-titania catalyst synthesized by a solid state method and waste cooking oil as reactant.

## II. METHODS AND MATERIAL

### 2.1 Materials and devices

The materials are classified into materials for catalyst preparation and biodiesel production. The reused silica-titania catalyst was obtained by washing the catalyst used in the previous reaction. The solvents used for catalyst preparation were hexane and methanol. The biodiesel production needed waste cooking oil, methanol, ethanol, KOH, and pp indicator [9].

### 2.2 Equipments

The equipments used in this study included equipment for synthesis and characterization. For synthesis, this study needed glassware, hot plate stirrer, oven, balance, thermometer, stirrer, centrifuge and fume hood. Instrument used for characterization of silica-titania catalyst was DR UV-Vis spectrometer while the biodiesel product was characterized by FTIR spectrometer.

### 2.2 Preparation and characterization of reused silica-titania catalyst

The reused silica-titania catalyst is originally the freshly prepared silica-titania catalyst that reapplied for next experiment denoted as "1<sup>st</sup> re-used" after once washing and applied again, and denoted as "2<sup>nd</sup>

re-used” after twice washing and applied again for next experiment. The re-used silica-titania catalyst was obtained by three time washing with 25 mL n-hexane and dried at room temperatur, and then washed by methanol, remained in a fumehood for a night to evaporate methanol. Furthermore, the given catalyst was dried in an oven for 2h at 105°C. After that, the given catalyst was cooled in a desiccant and followed by DR UV-Vis characterization in the wavelength range of 200 – 400 nm<sup>-1</sup> [11], [12]

Afterwards, the given catalyst was applied again in reaction of waste cooking oil to yield biodiesel. After the transesterification reaction finished, the given catalyst was separated and prepared again following the procedure as already mentioned above for the next transesterification reaction.

**2.3 Application of re-used silica-titania catalyst.**

The given catalyst after preparation was applied again for biodiesel production from waste cooking oil and methanol. The transesterification conducted in various temperatures of 50 – 70°C for 5h and catalyst loading of 7% with mol ratio of methanol to waste cooking oil of 6:1 [9].

Then the mixture was cooled after the reaction finished and followed by further process, i.e the separation of catalyst using a centrifuge. Further separation was done to remove excess methanol by heating above boiling point of methanol (64.7°C) [13].

**2.4 Catalytic activity**

The catalytic activity can be examined by assignment or analysis the biodiesel products through several tests for density, flow rate, acid number, and conversion, as well as FTIR characterization at wave number range of 600 – 4000 cm<sup>-1</sup>. Table 1 show sample labeling used in this study.

Table 1: Labels of biodiesel products from waste cooking oil (WCO) applying re-used silica-titania catalyst.

Labels of biodiesel products			
<i>1<sup>st</sup> reusability</i>		<i>2<sup>nd</sup> reusability</i>	
Temperatur e (°C)	Label	Temperatur e (°C)	Label
50°C	BCR1-50	50°C	BCR2-50
55°C	BCR1-55	55°C	BCR2-55
60°C	BCR1-60	60°C	BCR2-60
65°C	BCR1-65	65°C	BCR2-65
70°C	BCR1-70	70°C	BCR2-70

**III.RESULTS AND DISCUSSION**

**3.1 DR UV-Vis spectra of re-used silica-titania catalyst (re-used 1<sup>st</sup> and 2<sup>nd</sup>)**

Re-used catalyst has to show good stability, otherwise, loss of stability affects the catalyst performance and reduces its catalytic action. Therefore, an examination by DR UV-Vis is important to determine its titanium tetrahedral fraction in re-used silica-titania catalyst and compared to that of previous silica-titania catalyst. The deconvolution spectra of DR UV-Vis of re-used silica-titania catalyst (1<sup>st</sup> and 2<sup>nd</sup>) are illustrated in Figure 1 and Figure 2

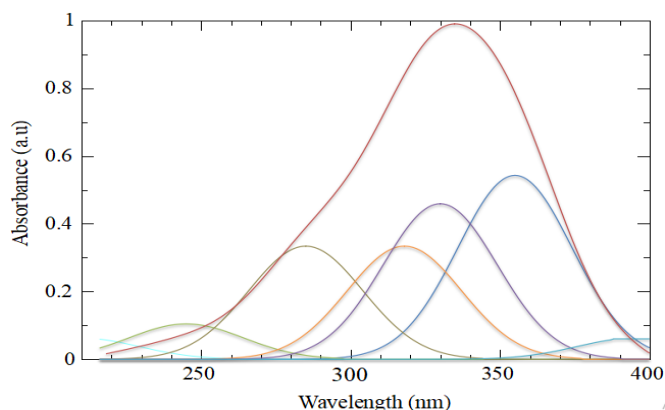


Figure 1: Deconvolution spectra of DR UV-Vis of re-used silica-titania (1<sup>st</sup>)

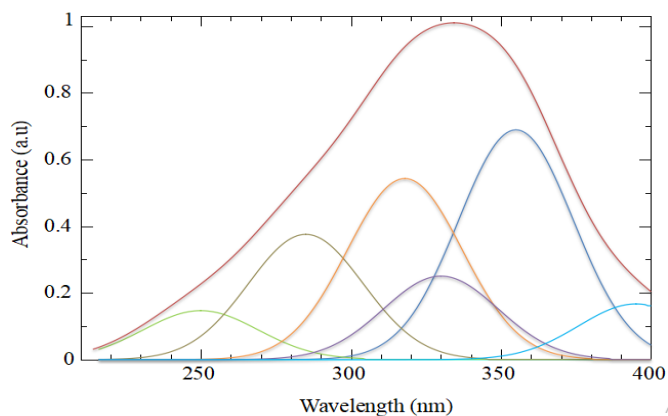


Figure 2: Deconvolution spectra of DR UV-Vis of re-used silica-titania (2<sup>nd</sup>)

Based on the deconvolution spectra of DR UV-Vis of re-used silica-titania (1<sup>st</sup>) shown in Fig.1 and re-used silica-titania (2<sup>nd</sup>) shown in Fig. 2, the results with respect to titanium tetrahedral coordination are found to be 24,98% and 24,65%, respectively. There is a reduction of titanium tetrahedral coordination as compared to that of previous silica-titania catalyst (31.04%) [14]

Nevertheless, the content of titanium tetrahedral coordination of re-used catalysts (1<sup>st</sup> and 2<sup>nd</sup>) are still higher than that of commercial TiO<sub>2</sub> (23%). This is probably corresponding with stability of Si-O-Ti bonding over temperature and time during the course of transesterification reaction. The stability of Si-O-Ti affected its catalytic action causing a reduction in percentage of conversion to biodiesel production [9]

Besides, it is also affected by phase transformation of anatase to rutile attributed to reduction of absorption peak of titanium tetrahedral coordination below 270 nm at deconvolution spectra of DR UV-Vis of re-used silica-titania catalyst. During the transesterification reaction, there was a destruction of Si-O-Ti bonding in some parts of catalyst molecule yielding formation of Si-O-Si and Ti-O-Ti bonding related to formation of less active titanium octahedral coordination. The structure of Ti-O-Ti can be found in both phases of anatase and rutile. In the wavelength range of 280-

300 nm the active anatase phase is more dominant, on the other hand, in the wavelength range of 330-400 nm the less active rutile phase is more remarkable [9]

### 3.2 FTIR spectra of biodiesel products.

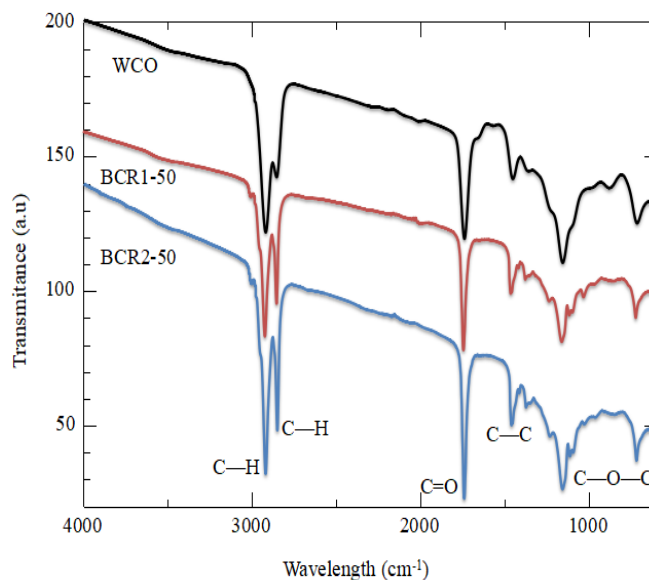


Figure 3: FTIR spectra of biodiesel products at optimum temperature (50°C).

The FTIR characterization of biodiesel products is based on the best results obtained from examination of biodiesel properties. The absorption peak at wave number of vibration (1300 – 1000 cm<sup>-1</sup>) is the main absorption peak of waste cooking oil and biodiesel products (50°C). At this area, there is an absorption peak of C-O ester from triglycerides and C-O from carboxyl fatty acid (Figure 3). The absorption peak of biodiesel is wider than that of waste cooking oil in the range of 1300-1000 cm<sup>-1</sup>. Several other absorption peaks at wave number of 1744 cm<sup>-1</sup> attributed to vibration of C=O bonding from ester, while a weak absorption peak at wave number 2922 cm<sup>-1</sup> attributed to -CH<sub>2</sub>.

Other main absorption peak at 1463 cm<sup>-1</sup> attributed to methyl ester group (CO-O-CH) and strengthened by an absorption peak of ester (C-O) at wave number of 1116 cm<sup>-1</sup>. There is a little difference of FTIR spectra between biodiesel and waste cooking oil due

to different chemical bonding in biodiesel and waste cooking oil.

Table 2: Significant absorption peaks of waste cooking oil (WCO) and biodiesel products

Type of bond	WCO absorption wave number (cm <sup>-1</sup> )	BCR1-50 absorption wave number (cm <sup>-1</sup> )	BCR2-50 absorption wave number (cm <sup>-1</sup> )
C=O	1742,81	1744.26	1744,16
C-H	2922,27	2922,70	2922,67
C-C	1455,67	1463,93	1463,90
C-O-C	1159,53	1463,93	1116.67

The data in Table 2 shows similarity in remarkable absorption peaks between waste cooking oil and biodiesel products. The similarity in absorption spectra between WCO and biodiesel is due to similar structure of functional group of triglycerides and methyl ester. The little difference between FTIR spectra of WCO and biodiesel is due difference in chemical bonding found on those chemical compounds.

### 3.3 Properties of biodiesel products

#### 3.3.1. Density and Viscosity (Flow rate)

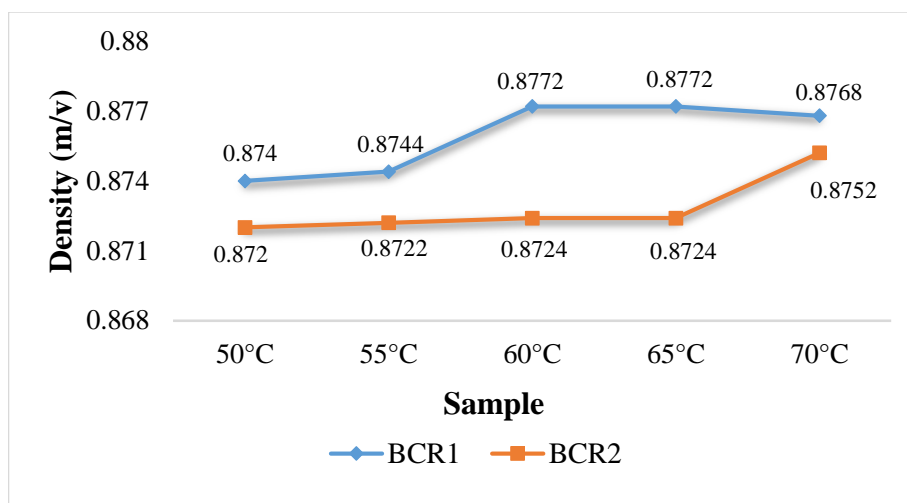


Figure 4: Density of biodiesel products at varied temperatures.

Figure 4 shows the density of biodiesel products at optimum temperature (50°C) applying re-used silica-titania catalyst (1<sup>st</sup> and 2<sup>nd</sup>) that were found lower than that of WCO. The density values of biodiesel products (50°C), i.e. 0.874 g/mL (BCR1-50) and 0.872 g/mL (BCR2-50), that are lower than that of WCO (0.879 g/mL) and then increased again at 70°. The elevation of density values is proportional with elevation of temperature in relation to glycerol content in biodiesel products and WCO. The incomplete separation of glycerol from biodiesel

yielded glycerol residue in biodiesel and strongly affected the density value [15]

The flow rate test can present the viscosity of fluids, which the flow rate is inversely proportional to viscosity, or in other words, the higher flow rate reflected the lower viscosity. Fig. 5 shows the flow rates of BCR1-50 and BCR2-50 at optimum temperature (50°C), i.e. 0.505 mL/s and 0.434 mL/s, respectively, that are higher than that of WCO (0.421 mL/s).

The temperature strongly affected the biodiesel production. Reduced temperature yielded lower flow

rate or higher viscosity, because the reaction is not too effective at low temperature. When the temperature is getting increased yielding increased reaction product due to much more energy supply.

However, when the temperature is too high resulting not effective reaction due to alcohol vaporized and probably soap formation [16]

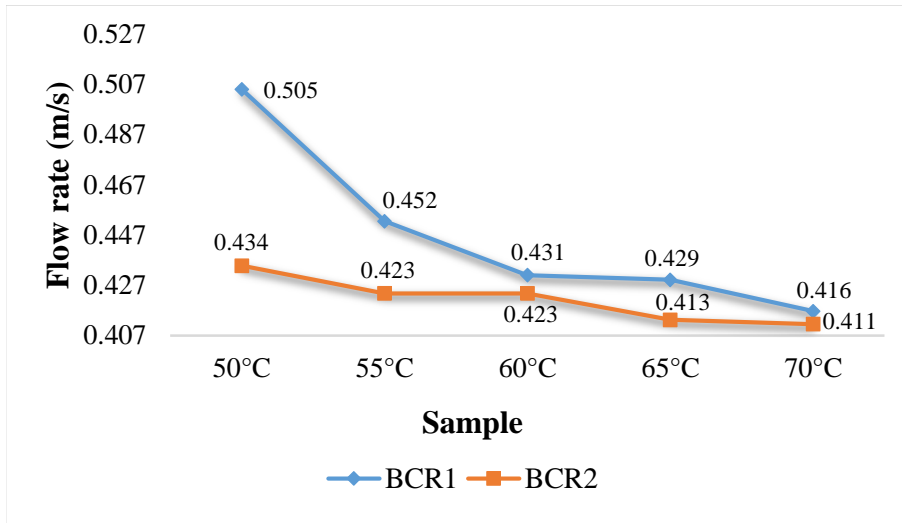


Figure.5: Flow rate of biodiesel products at varied temperatures

### 3.3.2. Acid number

The assignment of acid number is to determine the FFA content in biodiesel products. The acid number is determined by acid – base titration method. The

results of biodiesel conversion show that silica-titania catalyst is effective for WCO with high % FFA.

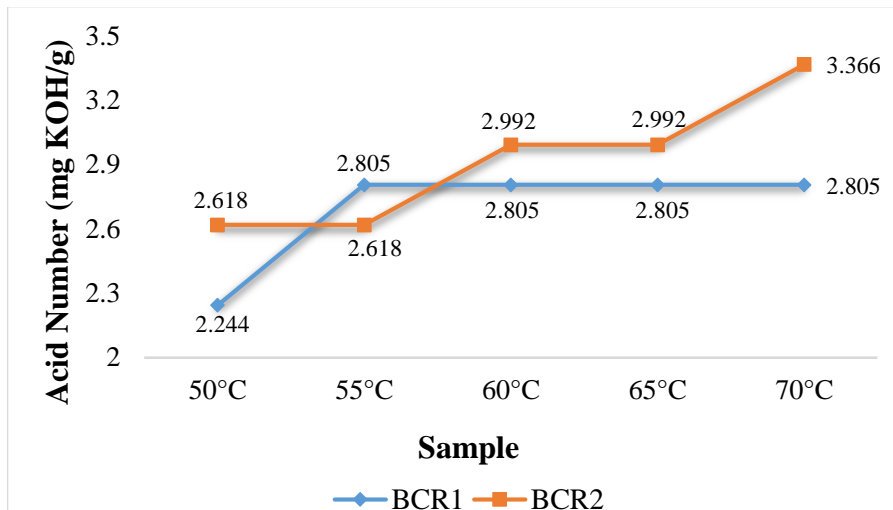


Figure 6: Acid number of biodiesel products

Figure 6 shows the acid number of biodiesel products and they are found to be lower than that of WCO (4.301 mg KOH/g) expressed in Table 3. The data of acid number can be used to determine the % FFA and

percentage of conversion of WCO to biodiesel products as seen in Table 4

Table 3: Acid number, % FFA, and % conversion applying re-used catalyst (BCR1)

Sample	Acid number	% FFA	% Conversion
WCO	4.301	2.1505	
50°C	2.244	1.122	47.82 %
55°C	2.805	1.4025	34.78 %
60°C	2.805	1.4025	34.78 %
65°C	2.805	1.4025	34.78 %
70°C	2.805	1.4025	34.78 %

Table 4: Acid number, % FFA, and % conversion applying re-used catalyst (BCR2)

Sample	Acid number	% FFA	% Conversion
WCO	4.301	2.1505	
50°C	2.618	1.309	39.13 %
55°C	2.618	1.309	39.13 %
60°C	2.992	1.496	30.43 %
65°C	2.992	1.496	30.43 %
70°C	3.366	1.683	21.73 %

Table 3 and Table 4 show that %FFA of biodiesel products are lower than that of WCO. The FFA content in the reactant like oil sources is substantial because it affects the reaction conversion. The high content of FFA has tendency for soap formation that in turn it reduced biodiesel product, because soap can hinder separation and purification process. More number of repeating the usage of silica-titania catalyst may decrease the conversion of vegetable oil to biodiesel.

The percentage of conversion to yield BCR1-50 and BCR2-50 are found to be 47.82% and 39.13%, respectively. This finding shows a reduction in catalytic action that is corresponding with reduction of titanium tetrahedral coordination and washing of catalyst due to repeatable usage of catalyst.

The examination of properties of biodiesel shows that silica-titania catalyst is reusable although its catalytic action decreased. Nevertheless, the application of re-

used silica-titania catalyst is still effective at optimum temperature (50°C) justified from increased flow rate and decreased density, as well as lower acid number of biodiesel products compared to that of WCO.

#### IV. CONCLUSION

The titanium tetrahedral coordination in silica-titania catalyst decreased after repeat usage of the given catalyst in biodiesel production from WCO. The optimum temperature in this study was found to be 50°C for respective production of BCR1-50 and BCR2-50.

#### V. ACKNOWLEDGMENTS

The author(s) would like to thank and express deepest gratitude to the Directorate of Research and Community Service of Universitas Negeri Padang, for their assistance in Research Funding, and also to Chemical Laboratory, Chemistry department, Faculty of Mathematic and Natural Science, Universitas Negeri Padang for supports and facilitations.

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**Cite this article as :** Fiona Rachma Annisa, Indang Dewata, Hary Sanjaya, Latisma Dj, Ananda Putra, Rita Sundari,Umar Kalmar Nizar , "Reusability test of Silica - Titania Catalyst on Biodiesel Production from Waste Cooking Oil in Various Temperatures", *International Journal of Scientific Research in Science and Technology (IJSRST)*, Online ISSN : 2395-602X, Print ISSN : 2395-6011, Volume 6 Issue 4, pp. 116-123, July-August 2019. Available at doi : <https://doi.org/10.32628/IJSRST196414>  
Journal URL : <http://ijsrst.com/IJSRST196414>