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Research Article

# Synthesis of $SrO.SiO_2$ Catalyst and Its Application in the Transesterification Reactions of Soybean Oil

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## Abstract

The synthesis and characterization of $SrO.SiO_2$ were carried out. The rice hull ash was utilized as a source for $SiO_2$. The $SrO.SiO_2$ was prepared by sol-gel technique, and the ratios of $SrO:SiO_2$ were varied as 0:1, 1:0, 3:2, 2:4, and 2:7. The sol-gel was calcined at 800 °C for 4 hours. The result was characterized using XRD and FTIR. The diffraction pattern shows that the diffraction angle was shifted, and the intensity of the main peaks was increased. This research indicated that the crystallinity of SrO was improved at the higher SiO content. Further, a new peak was observed in the IR spectra at a wavenumber of 900 $cm^{-1}$ indicating the appearance of new functional groups of the $SrO.SiO_2$. The catalytic activity of $SrO.SiO_2$ on transesterification reaction was optimized. The optimum condition was obtained at $SrO.SiO_2$ of 2:7, reaction time of 30 minutes, reaction temperature of 65 °C, the amount of catalyst of 1 % w/v of reactants, and the biodiesel yield of 96.66 %. Copyright © 2017 BCREC Group. All rights reserved

***Keywords***: Biodiesel; Catalyst; Soybean Oil; $SrO.SiO_2$; Transesterification

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## 1. Introduction

The development of biofuels (BBN) that is used to replace fossil fuel which is becoming scarce is continuously developed in Indonesia. One of the efforts that was made by the government is through Presidential Decree No. 5 of 2006 on national energy policy that is principled on the pricing policy, diversification, and energy conversion.

Various vegetable oils can be utilized as a new energy source that can be renewable and reliable. According to ISO (2012), biodiesel is defined as a biofuel in the form of methyl esters of fatty acids of vegetable oils. The vegetable oil will be in the transesterification should have acid numbers smaller than 1 [1] and soybean oil acid number is 0.84 [2]. Synthesis of biodiesel can be made through the transesterification reaction of triglycerides from vegetable oil with methanol using homogeneous catalysts, heterogeneous, and an enzyme catalyst. Homogeneous alkaline catalysts are typically used, such as NaOH solution, $NaOCH_3$, and KOH. The use of

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homogeneous catalysts bases produces some water that forms as a reaction between hydroxide and alcohol. The presence of water leads to an ester hydrolysis that produces soap through a saponification reaction and can reduce yields, thus require the separation process. Enzyme catalyst is expensive, and it can only react with short-chain alcohols and easily denatured. Therefore, heterogeneous catalysts are now much more developed than the homogeneous catalyst [2]. The SrO can accelerate many chemical reactions [3]. Biodiesel yield is 90 % in 20 minutes, and the SrO weakness is still homogeneous, so it is necessary to add a support such as $SiO_2$ [4]. The modification of SrO catalyst is made by formulating SrO with Musa Balbisiana Colla Underground Stem (MBCUS) to form agglomeration [5]. The result is used to synthesize biodiesel oils with a high free fatty acid level through esterification and transesterification reaction**.**

In this study, the catalyst was prepared by modifying SrO with $SiO_2$ from rice husk ash for biodiesel synthesis reaction of soybean oil. The result of synthesized catalyst was used for transesterification reaction of soybean oil. In the previous study, impregnation method was used for modification of catalyst, while in this study using the sol-gel method of the $SrO.SiO_2$ catalyst is purposed for improving catalytic activity and decrease the homogenous phase of SrO.

## 2. Material and Method

### 2.1. Material and instrumentations

The materials used in this research were waste cooking oil, potassium hydroxide (85.0 %, Merck), sodium hydroxide (99 %, Merck), ammonium hydroxide (25 %, Merck), hydrochloric acid (37 %, Merck), nitric acid (65 %, Merck), strontium nitrate (99 %, Merck), alcohol (95 %, Merck), methanol (99.8 %, Merck), and soybean oil.

The instruments used in this research were analytical balance (GR-200), hotplate magnetic stirrer (Yellow MAG HS 7), muffle furnace *(Barnstead Thermolyne 1400)*, hydrothermal reactor, oven *(Memmert)*, *centrifuge*, X-Ray diffraction (PW3 710, *Shimadzu* XRD *6000),* SEM (*Scanning Electron Microscope JEOL JSM-65101-A)*, Gas Chromatography Mass Spectrometry *(QP2010S Shimadzu), and* Infrared spectrometer (FTIR *Shimadzu-8201 PC*).

### 2.2. Experimentals

#### 2.2.1. Synthesis of $SrO.SiO_2$

The $SrO.SiO_2$ catalyst was conducted by the sol-gel method [6]. Silica sol-gel was made by adding 30 g silica powder to 1000 mL of 5 % NaOH; then it was stirred with a magnetic stirrer for 3 hours in a closed container without heating to form a silica sol. The silica sol was added by SrO dopants which were made by dissolving some $Sr(NO_3)_2.2H_2O$ in distilled water according to the composition of desideratum. The synthesis was done by various mole composition ratio of 3:2; 2:4; and 2:7. The mixture was stirred for 3 hours at a speed of 450 rpm to form a solution of strontium silicate. Then, a solution of $HNO_3$ 65 % was added slowly to the solution of strontium silicate to form a gel and then let it stand. After that, the solution was filtered and washed with distilled hot water. The gel was dried in an oven at 105 °C for 3 hours and then crushed to obtain powder strontium silicate. The powder was calcined at 800 °C for 4 hours and characterized.

#### 2.2.2. Characterization of catalyst

The $SrO.SiO_2$ catalyst was characterized by X-Ray Diffraction, FTIR, and SEM. The identification of $SrO.SiO_2$ crystal phase was conducted by Cu-Kα ($\lambda$ = 1.5405 Å) radiation at 40 kV and 30 mA, $2\theta = 0\text{-}90^o$ with a scan speed of 0.04 $^o$/second. The analysis of $SrO.SiO_2$ catalytic functional groups were done by FTIR using KBr film, and the spectrum was measured at the wavenumber of 4000-400 $cm^{-1}$. The observation of the catalyst surface was conducted using SEM (Scanning Electron Microscope JEOL JSM-65101-A).

The characterization of biodiesel was carried out by using Gas Chromatography to find out the optimization of catalyst compositions, whereas the GC-MS was used to determine the types of methyl ester groups. The identification of functional groups of methyl ester was carried out by FTIR.

#### 2.2.3. Synthesis of biodiesel from soybean oil

The synthesis of biodiesel was carried out through a transesterification reaction. The transesterification reaction was conducted by mixing the reactants of oil and methanol in the ratio of 1: 4 and the catalyst of 1 % w/v. The reaction was conducted with various ratios of SiO:SrO (0:1, 1:0, 3:2; 2:4, and 2:7), and variations of reaction time of 30, 60, 90, and 120 minutes. These experiments were carried out by refluxing the mixture at a temperature of 65 °C with stirring a speed of 300 rpm for 30 minutes and let it stand for 24 hours. Then, it was filtered to separate the catalyst from the reaction product. The biodiesel reaction products were tested for density, viscosity and the refractive index to determine the quality of biodiesel product and analyzed by using GC-MS to determine the type of methyl ester formed. The biodiesel level was calculated based on the amount of chromatogram area of methyl ester which was the result of GC-MS compared to the entire area of the chromatogram. Total biodiesel is calculated by comparing the total number of moles of methyl ester which is formed by the number of moles of first oil.

## 3. Results and Discussion

Heterogeneous catalysts are usually used in the transesterification reaction of soybean oil with alcohol [2]. The result of the synthesis of silica is shown in Figure 1. Figure 1 shows (a) the formation of silica sol-gel, (b) gel of $SrO.SiO_2$, and (c) $SrO.SiO_2$ powder that was calcination product. The gel (b) still has a large water content so that it is necessary to eliminate the moisture content of the material by calcination 800 °C to obtain the optimum catalyst. The result of catalyst diffractogram from the synthesis is shown in Figure 2. The SrO is indicated by the emergence of peak 2θ of $29.77^{o}$; $34.69^{o}$; $49.88^{o}$, and $59.33^{o}$. This pattern is almost similar to previous literature [7]. The SrO catalyst is indicated by the emergence of peak 2θ of $29.64^{o}$; $34.65^{o}$, and $49{,}95^{o}$ [7]. The crystallinity level is similar to JCPDS library. The $SiO_2$ diffractogram pattern in this study is shown by the emergence of peak 2θ of $21.18^{o}$; $26.96^{o}$; and $31.31^{o}$ which is similar to previous literature [8]. The $SiO_2$ component appears at the 2θ peak of $21.18^{o}$ which is a polymorph silica tridymite. The 2θ of $26.96^{o}$ shows quartz, while the 2θ peak of $31.31^{o}$ shows a cristobalite [8]. The $SiO_2$ diffractogram in this study indicates the widening peak at 2θ of 20-23 $^{o}$. The $SiO_2$ component is amorphous as it widens peak at 2θ of 21-22 $^{o}$ [9]. A raising crystallinity is very important about the catalytic properties [10].

The $SrO.SiO_2$ (3:2) catalyst has SrO peak at 2θ of $29.83^{o}$, $34.63^{o}$, $50.47^{o}$, $59.97^{o}$, and $SiO_2$ peak at 2θ of $21.66^{o}$, $26.79^{o}$, $35.42^{o}$, and $38.67^{o}$, the $SrO.SiO_2$ (2:4) catalyst has peak of SrO at 2θ of $29.90^{o}$, $34.67^{o}$, $50.52^{o}$, $59.94^{o}$, $SiO_2$ peak at 2θ of $21.74^{o}$, $26.60^{o}$, $34.67^{o}$, $38.72^{o}$, and $SrO.SiO_2$ (2:7) catalyst has SrO peak at 2θ of $30.00^{o}$, $34.769^{o}$, $49.98^{o}$, and $SiO_2$ peak at 2θ of $21.84^{o}$, $26.95^{o}$, and $40.17^{o}$ [7,8].

The infrared spectra of the catalyst are shown in Figure 3. The crystallinity of SrO increased as the addition of $SiO_2$ shifting the diffraction angles. High calcination temperature increases purity catalyst from various dirt [12]. The shift angle was occurred due to the effect of treatment into the SrO catalyst modified by $SiO_2$.

The SrO catalyst is shown at the peak of 966 $cm^{-1}$ that is a Sr–O bond. This pattern is similar to a research by Pavlyuchenko, in which the Sr–O functional groups appears at the wavenumber of 700-1000 $cm^{-1}$ [12]. The SrO appears at 900 and 950 $cm^{-1}$ [12]. The peak at 1460 $cm^{-1}$ indicates –OH bending vibration that still allows the formation of Sr(OH). Meanwhile, the $SiO_2$ has a width and a sharp absorption in 1095 $cm^{-1}$ that indicates Si–O symmetric stretching vibration of the Si–O–Si. The peak of 1633 $cm^{-1}$ indicates –OH bending


(a) (b) (c)

**Figure 1.** Results of catalyst synthesis of catalysts rice hull ash: (a) silica sol which was added by solution of dopant, (b) gel of $SrO.SiO_2$, (c) powder of $SrO.SiO_2$

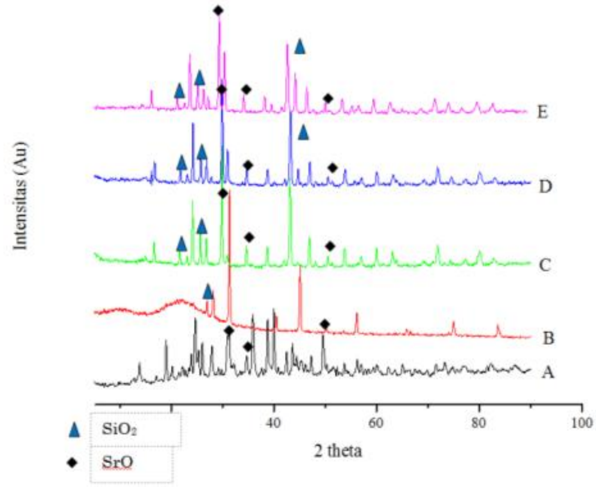

**Figure 2.** Diffractogram of catalyst: (A) SrO, (B) $SiO_2$, (C) $SrO.SiO_2$ 3:2, (D) $SrO.SiO_2$ 2:4, (E) $SrO.SiO_2$ 2:7

vibration from Si–OH. The peak at 798 cm$^{-1}$ indicates Si–O symmetric stretching vibration of Si–O–Si, while the absorption pattern in 479 cm$^{-1}$ shows Si–O–Si bending vibration. The $SiO_2$ pattern in this research has similarity to previous literature [13]. At wavenumber of 1635 cm$^{-1}$ indicates –OH bending vibration of Si–OH [14]. The pattern of 794 cm$^{-1}$ indicates Si–O symmetric stretching vibration from Si–O–Si, and the absorption pattern of 470 cm$^{-1}$ shows Si–O–Si bending vibration.

Based on Figure 3, it can be understood that the functional groups in the catalyst modification of $SrO.SiO_2$ (3:2) of 1477 cm$^{-1}$ indicates –OH bending vibration of Si–OH. The pattern of 1074 cm$^{-1}$ indicates Si–O symmetric stretching vibration from Si–O–Si. The peaks at 972 cm$^{-1}$ and 928 cm$^{-1}$ indicate Sr–O. The peak at 706 cm$^{-1}$ indicates Si–O symmetric stretching vibration of Si–O–Si. The $SrO.SiO_2$ catalysts (2:4) is showed by the peak of 1632 cm$^{-1}$ indicating –OH bending vibration within Si–OH. The peak at 1075 cm$^{-1}$ indicates Si–O symmetric stretching vibration of Si–O–Si. The peak at 970 cm$^{-1}$ and 925 cm$^{-1}$ indicate Sr–O, while the peak at 703 cm$^{-1}$ indicates Si–O symmetric stretching vibration of Si–O–Si. Based on the analysis of functional groups on SrO, $SiO_2$, and $SrO.SiO_2$ from infrared spectral data, a new peak of 900 cm$^{-1}$ indicating that SrO catalysts have been successfully modified with $SiO_2$.

The optimum catalyst characteristic was carried out by Scanning Electron Microscope. The $SrO.SiO_2$ catalyst ratio of 2:7 is shown in Figure 4 (a) 3000x magnification and Figure 4 (b) 5000x magnification. The surface morphology of $SrO.SiO_2$ shows agglomeration. The lumps or agglomeration structure shows their metal oxides that formed on the treatment of the catalyst [14].

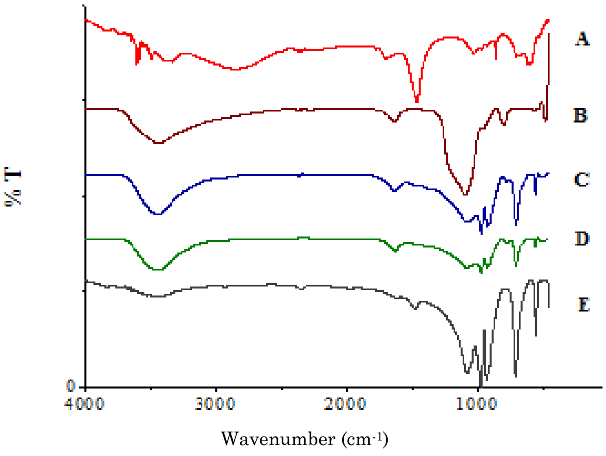

**Figure 3.** Results of infrared spectra of catalysts: (A) SrO, (B) $SiO_2$, (C) $SrO/SiO_2$ 3:2, (D) $SrO/SiO_2$ 2:4, (E) $SrO/SiO_2$ 2:7

Figure 5 shows percentage of product concentration from the catalyst. The addition of more $SiO_2$ increases the percentage of product concentration. This is due to the influence of $SiO_2$ which functions as a buffer. The buffer causes the active component of the catalyst that was dispersed evenly, improving mechanical strength, spreading reaction heat and improving the stability of the catalyst [14]. The optimum results were obtained at $SrO.SiO_2$ 2:7.

Figure 6 shows the percentages of products concentration of methyl ester. The products are methyl linoleic, methyl elaidic, and methyl linolenic. The optimum ratio of oil and methanol is 1:12, in which the higher methanol ratio converts fatty acid into methyl ester whereas the ratio of oil and methanol of 1:4 tends to a little methyl ester [3]. The optimum condition is obtained with a reaction time of 30 minutes.

Figure 7 indicates the soybean oil contents where a peak at wavenumber of 723 cm$^{-1}$ shows the band of =CH, while peaks at 1100, 1163, and 1239 cm$^{-1}$ indicate the CO group of

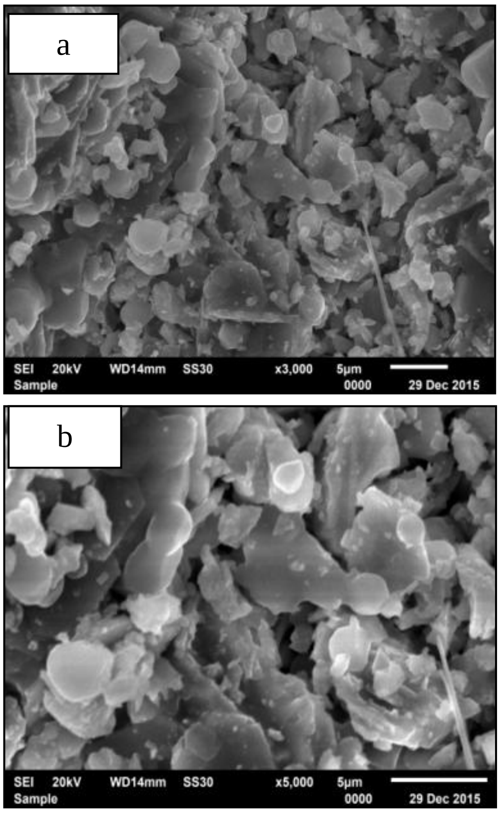

**Figure 4.** SEM characterization of $SiO.SiO_2$ 2:7 (a) 3000x magnification, (b) 5000x magnification

esters that usually appears at the wavenumber of 1050-1300 cm$^{-1}$. The wavenumber of 1378 cm$^{-1}$ indicates the presence of functional groups of C–H$_3$, while the wavenumber of 1463 cm$^{-1}$ indicates the presence of methylene functional group of –CH$_2$–. The peaks at the wavenumbers of 2855 and 2927 cm$^{-1}$ show the CH functional groups that usually appears a peak at the wavenumber of 2850-2970 cm$^{-1}$. The peak at wavenumber of 1747 cm$^{-1}$ indicates the C=O functional groups of the ester that appears at the wavenumber of 1690-1760 cm$^{-1}$ [2].

Biodiesel production from soybean oil over catalysts of SrO, SiO$_2$, and SrO.SiO$_2$ appears at peaks of 1053, 1112, 1172, 1197, and 1245 cm$^{-1}$ indicating the CO group of ester that usually appears at the wavenumber of 1050-1300 cm$^{-1}$.

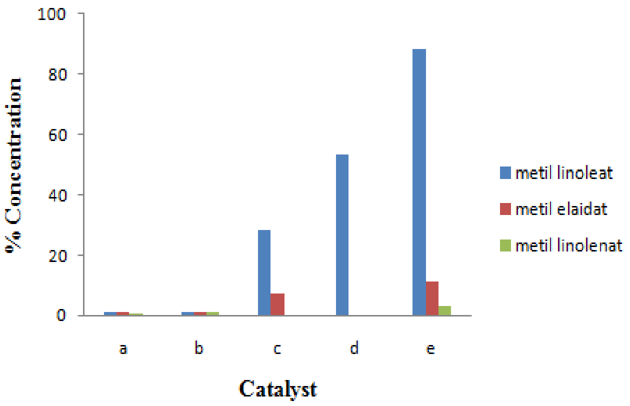

**Figure 5.** Relations of the percentage of the catalyst concentration: (a) SiO$_2$ (b) SrO (c) SrO:SiO$_2$ 3:2 (d) SrO:SiO$_2$ 2:4 (e) SrO:SiO$_2$ 2:7, at a temperature of 65 °C during the 30 minutes, the catalyst weight of 1 % w/v of oil, the ratio of oil:methanol of 1:4

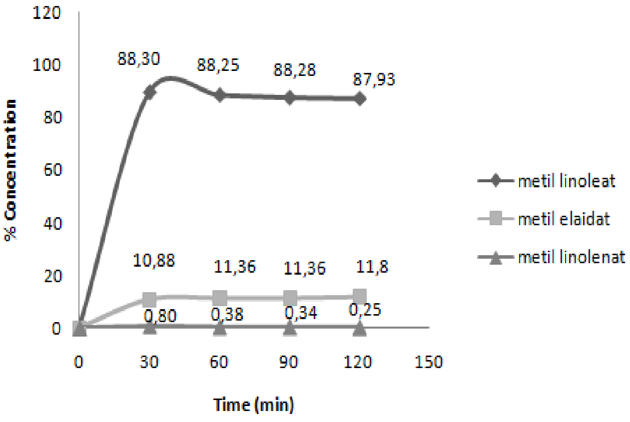

**Figure 6.** Relations of reaction time with the percentage of the product concentration, at a temperature of 65 °C with a SrO.SiO$_2$ 2:7 catalyst 1 % w/v of reactants, the ratio of oil: methanol of 1:4

The peaks at 1363 and 1459 cm$^{-1}$ indicates a C–H$_3$ functional groups that usually appear a peak at the wavenumber of 1340-1470 cm$^{-1}$. The CH functional groups appear at peaks of 2855 and 2928 cm$^{-1}$ that usually appear at the peak of 2850-2970 cm$^{-1}$. The peak at wavenumber of 1744 cm$^{-1}$ indicates the functional groups of C=O of the ester that usually appears at the wavenumber of 1690-1760 cm$^{-1}$ [2]

The biodiesel chromatogram is shown in Figure 8 indicates presence of a methyl ester, and interpretation of chromatograms is shown in Table 1. Figure 8 and Table 1 show the products from the transesterification reaction which are methyl palmitate, methyl elaidic, methyl linoleic and methyl linolenic and the biodiesel yield 96.66 %.

Table 2 shows the physical characteristics of biodiesel that have a density, kinematic viscosity and the refractive index by SNI 04-7128-2006.

**Table 1.** Results of GC-MS chromatogram interpretation biodiesel

| Compound | Retention time (minutes) | Concentration (%) |
|---|---|---|
| Methyl palmitate | 33.75 | 15.08 |
| Methyl elaidic | 40.01 | 19.90 |
| Methyl linoleic | 41.83 | 57.37 |
| Methyl linolenic | 44.34 | 7.65 |
| Total methyl ester | | 100.00 |

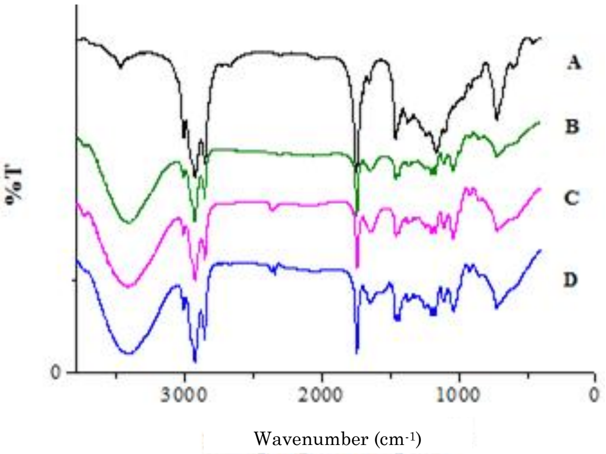

**Figure 7.** Results of biodiesel infrared spectra (A) soybean oil, (B) biodiesel SiO$_2$, (C) biodiesel SrO, (D) biodiesel SrO.SiO$_2$ 2:7

## 4. Conclusions

The characteristics of SrO.SiO$_2$ catalyst showed the increase of crystallinity level of SrO in line with the increase of SiO$_2$ and shift in the diffraction angle that showed the modification on SrO.SiO$_2$ catalyst. The functional groups of SrO.SiO$_2$ catalyst was marked by the appearance of a new peak in the catchment concentration of about 900 cm$^{-1}$. The surface morphology of SrO.SiO$_2$ catalyst had lumps or agglomeration structure indicating metal oxides SrO and SiO$_2$. The optimum condition of transesterification reaction is when using the SrO.SiO$_2$ 2:7 catalyst, a reaction time of 30 minutes, the temperature of 65 °C, the amount of catalyst used 1 % of total weight, and biodiesel yield of 96.66 %.

## References

[1] Purwaningsih, E., Supartono, Harjono. (2012). Transesterification Reaction Coconut Oil with Methanol Using Bentonite Catalysts. *Indonesian Journal of Chemical Science*. (2): 1-7.

[2] Istadi, I., Rahmawati, D.A., Intaningrum, D. (2013). Synthesis and Characterization of Heterogeneous Catalysts $SO_4^{2-}$-ZnO and $SO_4^{2}$/ZnO by Coprecipitation Method and Impregnation for Biodiesel Production of Soybean Oil. *Jurnal Teknologi Kimia dan Industri*, 2(4): 243-252.

[3] Liu, X., Huayang, H., Yujun, W., Shenlin, Z. (2007). Transesterification of Soybean Oil to Biodiesel Using SrO as a Solid Base Catalyst. *Catalyst*, (8): 1107-1111.

[4] Chang, Jo-S., Ching, C., Chien, H., Dang, T. (2012). Biodiesel Synthesis via Heterogeneous Catalysis Using Modified Strontium Oxides as the Catalysts. *Bioresource Technology* (113): 8-13.

[5] Kumar, P., Sarma, A.K., Bansal, A., Jha, M.K. (2016). Formulation of SrO-MBCUS Agglomerates for Esterification and Transesterification of High FFA Vegetable Oil. *Bulletin of Chemical Reaction Engineering & Catalysis*, 11(2): 140-150

[6] Pandiangan, P., Kamisah D., Simanjuntak W. (2013). Synthesis of Heterogeneous Catalysts Rice Husk MgO-SiO$_2$ Sol-Gel Method And Its Application In transesterification reactions Coconut Oil, *Proceedings of National Converence Science and Technology*: 516-524.

[7] Haq, I.A., Widiarti, N., Mahatmanti, F.W. (2015). Biodiesel Synthesis from Waste Cooking Oil Using CaO.SrO Catalyst by Transesterification Reaction in Batch. *Indonesian Journal of Chemical Science*, (2): 1-7.

[8] Suka, I. G., Simanjuntak W., Simon S., Evi T. (2008). Rice Husk Silica Characteristic of Lampung obtained from Extraction Method., *Journal of Mathematics and Natural Sciences*, 37(1): 47-52.

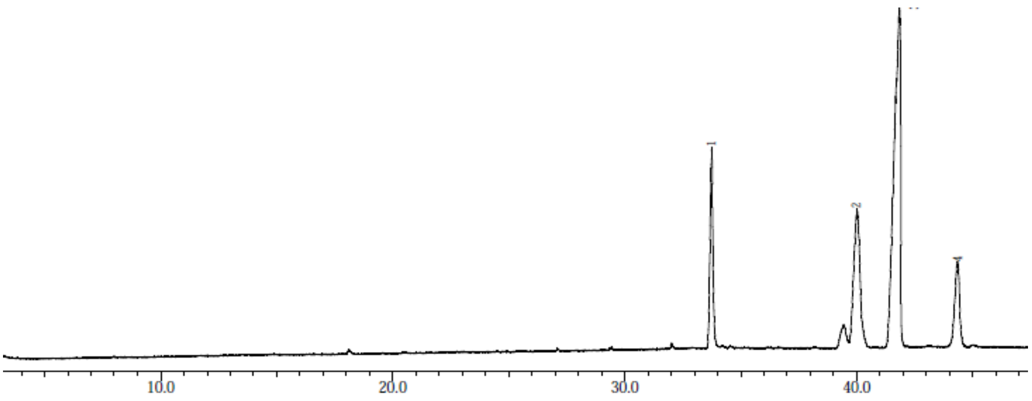

**Figure 8.** The chromatogram of biodiesel synthesis results with SrO:SiO$_2$ ratio of 2:7, at 30 minutes and temperature of 65 °C, oil to methanol ratio of 1:4, (1) methyl palmitate, (2) methyl elaidic, (3) methyl linoleic,(4) methyl linolenic

**Table 2.** Test data of physical characterization of biodiesel synthesis results

| Characterization | Soybean Oil | Biodiesel | Source of Biodiesel Standards |
|---|---|---|---|
| Density (g/mL) | 0.88 | 0.85 | 0.85-0.89 (SNI 04-7128-2006) |
| Viscosity (cSt) | 19.25 | 2.41 | 2.3-6.0 (SNI 04-7128-2006) |
| Refractive index | 1.4 | 1.3 | 1.3-1.4 (SNI 04-7128-2006) |

[9] Kalapathy, U., Proctor, A., Shultz, J. (2000). A Simple Method for Production of Pure Silica from Rice Hull Ash. *Bioresource Technology,* (73): 257-262.

[10] Irvantino, B., Wahyuni, S., Pranoto, S.H. (2013). Preparation of Catalyst Ni/ZAA by Sonochemical Method for Catalytic Cracking Polypropylene and Polyethylene. *Indonesian Journal of Chemical Science,* (2): 1-7.

[11] Zhu, H., Zongbin, W., Yuanxiong, C., Ping, Z., Shijie, D., Xiaohua, L., Zongqiang, M. (2006). Preparation of Biodiesel Catalyzed by Solid Super Base of Calcium Oxide and Its Refining Process. *Chinese Journal of Catalysis*, 27(5): 391-396.

[12] Nayebzadeh, H., Saghatoleslamia, N., Maskooki, A., Vahida, B.R. (2013). Effect of Calcination Temperature on Catalytic Activity of Synthesis SrO/S-$ZrO_2$. Chemical and Biochemical. *Engineering Quarterly*, 27(3): 267-273.

[13] Yusrin, A.F., Eko, B.S., Widhi F.M. (2014). Comparison of the ability of silica gel from coconut husk ash with rice husk ash to a reduction of heavy metal ions $Cd^{2+}$. *Indonesian Journal of Chemical Science* (2): 1-7.

[14] Lestari, S.P., Hadiyanto. (2015). Potential Shellfish as Catalyst for Making Biodiesel. *Proceedings of National Seminar of Chemical Engineering*, 1-6

*Selected and Revised Papers from The 2nd International Seminar on Chemistry (ISoC 2016) (Surabaya, 26-27 July 2016) (http://chem.its.ac.id/isoc-2016/) after Peer-reviewed by Scientific Committee of ISoC 2016 and Peer-Reviewers of BCREC journal*