JBAT 7(2) (2018) 136 – 141
p-ISSN 2303 0623
e-ISSN 2407 2370

Jurnal Bahan Alam Terbarukan

Terakreditasi: SK No.: 36b/E/KPT/2016
http://journal .unnes.ac.id/nju/index.php/jbat

Biodiesel Synthesis From Waste Cooking Oil Using CaO.SrO Catalyst By Transesterification Reaction In Batch Reactor

Nuni Widiarti✉, Ismi Arinal Haq, F. Widhi Mahatmanti, Harjito, Cepi Kurniawan, Suprapto, Didik Prasetyoko

DOI 10.15294/jbat.v7i2.14925

Chemistry Department,Faculty of Mathematics and Science, Universitas Negeri Semarang, Semarang, 50229 Indonesia

Article Info

Article history:
Received
July 2018
Accepted
November 2018
Published
December 2018

Keywords :
Biodiesel;
Catalyst;
Transesterification;
Coprecipitation

Abstract

CaO is a very good catalyst for oil transesterification reactions into biodiesel, but requires a reaction time of 2 hours to obtain equilibrium. The time of CaO catalysis reaction can be accelerated by modifying the CaO catalyst with SrO. Synthesis biodiesel of waste cooking oil has been successfully conducted by transesterification reaction that used batch reactor assisted by CaO.SrO catalyst. The aim of this study is to determine the characteristics and catalytic activity of catalyst in the transesterification reaction. Catalysts have been successfully synthesized by coprecipitation method with oil to methanol molar ratio of 1:1, and its calcined at 800°C for 3 hours. Catalyst was characterized by XRD to determine the crystallinity. The smaller catalyst crystallinity obtained as the decline in intensity and shifts diffraction angles of CaO modified SrO catalyst. Surface area of catalyst characterized by SAA, that allow surface area between CaO modified SrO by 10.217 m^2/g. Transesterification reaction performed on variation time (30, 60, 90, 120, 150 minutes), and the catalysts amount (1, 2, 4, 6, 8% $^{w}/_{v}$). The optimum condition of catalytic activity in reaction for 2 hours and the catalyst amount is 1% $^{w}/_{v}$ of reactants that produce yield of biodiesel is 96.4%.

INTRODUCTION

Biodiesel is based on the methyl ester vegetable oil, just like the waste cooking oil from palm oil. Ketaren (2005) stated that waste cooking oil has FFA content for 5-15%, for the transesterification reaction can be conducted, then the FFA number has to be decreased until < 1%, as the transesterification reaction lasts between the vegetable oil (which FFA <1%) with metanol using heterogeneous base catalyst (Hambali et al., 2007). Heterogeneous base catalyst that can be used in transesterification, that is metal oxide with the catalytic activity order BaO > SrO > CaO > MgO (Liu et al., 2007). Liu et al. (2008) reported that CaO is one of the heterogeneous catlysts that is mostly used beacuse it has a high catalytic activity. CaO can be used as a heterogeneous catalyst with a slow reaction speed and it costs 2 hours reaction to reach a balance condition (Liu et al., 2008). Liu et al. (2007) revealed that the SrO catalytic activity order is higher than BaO, proved in the transesterification of soybean oil to biodiesel, the result of biodiesel is over 95% in 30 minutes.

The catalytic activity of heterogeneous catalysts can be increased by increasing the concentration of the active side surface, for example modification of the CaO catalyst with SrO by the coprecipitation method. This synthesis method equal with the making of ZnO catalyst by Kanade et al. (2006) and the modification follows Ngamcharussrivichai et al. (2008). So, hopefully this CaO.SrO catalyst can form a biodiesel with a

---

✉Corresponding author:
Chemistry Department,Faculty of Mathematics and Science
Universitas Negeri Semarang, Semarang, 50229 Indonesia
E-mail: nuni_kimia@mail.unnes.ac.id

ISSN 2303-0623
e-ISSN 2407-2370

$$Ca(CH_3COO)_2.2H_2O_{(l)} + Sr(NO_3)_2.2H_2O_{(l)} + 2C_2H_2O_4.2H_2O_{(l)} \rightarrow CaC_2O_4.2H_2O_{(s)} + SrC_2O_4.2H_2O_{(s)} + 2CH_3COOH_{(l)} + 2HNO_{3(l)} + 2H_2O_{(l)} \quad (1)$$

$$CaC_2O_4.2H_2O_{(s)} + SrC_2O_4.2H_2O_{(s)} \overset{\Delta}{\rightarrow} CaCO_{3(s)} + SrCO_{3(s)} + 2CO_{(g)} + 4H_2O_{(l)} \quad (2)$$

$$CaCO_{3(s)} + SrCO_{3(s)} \overset{\Delta}{\rightarrow} CaO_{(s)} + SrO_{(s)} + 2CO_{2(g)} \quad (3)$$

high yield reaching more than 90% and a short reaction time.

RESEARCH METHODOLOGY

The instruments used in this research are AND GR-200 analytic balance, Hotplate magnetic stirrer, furnace, hydrothermal reactor, memmet oven,centrifuge,Gas Chromatography (GC) Hawllett Packard 5890 Series II, Gas Chromatography-Mass Spectroscopy (GC-MS) Perkin Elmer Clarus 680SQ 8T, instrument X-Ray Diffraction Phillips Expert (XRD) Philips pW 1800, Quantachrome Instruments Nova 1000e.

The materials used in this research are waste cooking oil, aquades, whatman 42 paper, filter paper, deionize water, activated charcoal adsorbent, 95% alcohol, and material with grade pro analysis that is Phenolphthalein Indicator (PP), metanol, oxalate acid ($H_2C_2O_4.2H_2O$), Sr Nitrate ($Sr(NO_3)_2.2H_2O$), Ca Acetate ($Ca(CH_3COO)_2.2H_2O$), NH_4OH liquid, $CO(NH_2)_2$ (Urea Anhydrate), acetone (CH_3COCH_3), NaOH, KOH.

This research was conducted in 5 steps, the first step was doing a pretreatment to the waste cooking oil that would be used in the transesterification, in the second step, the catalyst was synthesized with molar ratio of CaO.SrO (1:1)using precursor Ca acetate and Sr nitrate in a hydrothermal reactor and the result was calcined at 800°C for 3 hours. The third step was the characterized of CaO.SrO (1:1) catalyst using *X-Ray Diffractometer* (XRD) to determine the crystallinity of the catalyst, also using *Surface Area Analyzer* to determine the catalyst surface area with *Brunauer-Emmet-Teller*(BET)method. The forth step was doing a biodiesel synthesis with the time variance of (30, 60, 90, 120, and 150 minutes) and the amount of CaO.SrO 1:1 catalyst (1, 2, 4, 6, and 8% b/vto the reactant). The reaction was conducted at 65°C, the mixing speed of 300 rpm, and the the volume of oil:metanol (1:3). The fifth step was identifying the result of biodiesel synthesis and physical characterize of biodiesel. The identification of the biodiesel synthesis result using instrumentation of Gas Chromatography-Mass Spectroscopy (GC-MS) to determine the concentration of the methyl ester content in biodiesel, and the result of biodiesel physical characterize was adjusted with SNI 04-7182-2006 tested in density, viscosity, and bias index.

RESULTS AND DISCUSSION

The pretreatment of the waste cooking oil was conducted using 3 steps reaction, that is *despicing* (flavor removal), neutralization, and *bleaching* (color removal) according to Siswani et al. (2012). The pretreatment was conducted to reduce the value number of acid in the waste cooking oil as the domestic waste product. The number of acid oil before the pretreatment was conducted was 4.867 mgKOH/gr, and after the pretreatment, the value number decreased to 0.562 mgKOH/gr. The result of the acid number decreasing showed a success in the pretreatment of waste cooking oil and then the pretreatment oil product was synthesized with transesterification assisted by CaO.SrO (1:1) catalyst.

The synthesis of CaO.SrO (1:1) catalyst was conducted using coprecipitation method with oxalate acid as the acid precipation agent. The precursor used was Ca acetate ($Ca(CH_3COO)_2.2H_2O$) and Sr nitrate ($Sr(NO_3)_2.2H_2O$). the synthesis began with making calcium acetate liquid and strontium nitrate by dissolving each solid to the deionize water until a liquid was obtained with the molar ratio 1:1, then oxalate acid was added in the liquid until a turbid liquid was obtained. The change of liquid from pure to turbid showed that the liquid had saturated and indicated that calcium-strontium oxalate was formed. The reaction happened in the coprecipitation as shown by Kanade *et al.* (2006) is shown in Eq. (1) – (3).

Those reaction equation was a decomposition reaction from calcium oxalate and strontium oxalate solid to calcium oxide and strontium oxide solid with calcination treatment in a high temperature according to (Rahmawati *et al.*, 2012). The calcination process also affected in the decomposition of acid oxalate to H_2O and CO_2, like the decomposition of acid oxalate as reported by Barokah & Widiarti (2015) so it did not leave pollutant in the ZnO and CuO/ZnO. CaO.SrO catalyst as a synthesis product had a X-ray difraction pattern in Figure 1. The difraction pattern in Figure 1 showed that CaO.SrO catalyst was a crystalline catalyst, marked with the high and sharp peaks in the angle 2θ = 15-65°, also it showed that in the CaO.SrO sample had drifaction peaks which was similar with the difraction pattern in the CaO dan SrO sample.

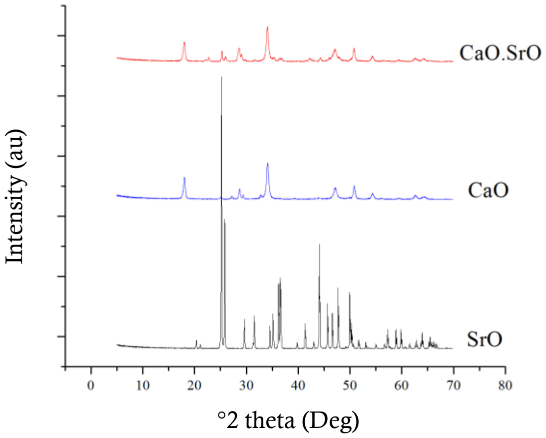

Figure 1. Difactogram pattern of CaO, SrO, and CaO.SrO (1:1) catalyst

The difraction peak of CaO as the calcination product at 800°C for 3 hours was in 2θ = 32.780° and 64.350° and the peak of SrO appeared in 2θ = 25.202° ; 29.643° ; 34.650° and 49.952°. The difraction peak combination of CaO.SrO was also showed with the angle of = 25.223° ; 29.790° ; 31.687° ; 59.478° ; 62.638° ; 64.192°in which the intensity was displaced and reduced. The increase of crystallinity that was obtained after the modification process become less maximal because the calcination temperature was less maximal so the hydration and recarbonation happened to the catalyst. The calcination in the less maximal temoerature can only reach the pore surface of the catalyst, to increase the purity of the catalyst from the higher pollutants and did not damage the catalyst structure. A calcination was needed at 900°C or above (Zhu et al., 2006).

The characterized of surface area with the nitrogene adsorption was conducted to the CaO, SrO, and CaO.SrO (1:1) samples. The result of surface area measurement with the BET method from CaO, SrO, and CaO.SrO (1:1) catalyst was 11.400 m^2/g, 1.802 m^2/g, and 10.217 m^2/g. The test result of CaO.SrO sample showed that a combination was occured between CaO modified by SrO, and produced CaO.SrO surface area that was 5.6 times bigger than the pure SrO. The CaO catalyst had a surface area 1.2 times bigger than CaO.SrO catalyst, this result showed that modifying CaO with Sr species affected the surface area of CaO and helped to disperse Sr species to the whole surface of CaO. Yoosuk *et al.* (2010) stated the similar thing that Sr species can be dispersed to the entire surface of MgO so it brought MgO.SrOcatalyst a bigger surface area than the pure SrO.

The test of catalytic activity in the CaO.SrO (1:1) sample in transesterification reaction of waste cooking oil to biodiesel using reactor batch method with the time variance and catalyst amount, to determine the optimum condition from the test of catakytic activity and the result was analized with gas chromatography. The result of optimum transesterification reaction in the time variace showed in the 120 minutesand the product area percentage for 0.479%. The optimum reaction time achieved because the product area percentage increased along with the duration of reaction and would decrease after it reached a balance reaction, so with the increase of reaction time it would not favorable because it did not increase the result (Azmi, 2009).

The optimum reaction time would conduct a further reaction with a variation of catalyst amount and product area percentage produced for 2.484% in the use of 1% b/v catalyst amount to the optimum reactant. The product area percentage continued to decrease as the catalyst amount increased. The transesterification reaction that is given a treatment of increasing catalyst amount showed there was a problem in the contact (collision) between molecule, because the given catalyst would precipitate and coagulate in the base of reaction gourd. This statement was proven by Wendi et al. (2015) who stated that the effect of the increase of catalyst amount, the combination of catalyst and reactant had become too thick, so it cause trouble in the mixing and demanding of higher power consumption for the mixing. The problem would also affect the catalytic activity from the used catalyst decreased as the decreasing of catalyst active side function, and the adsorption process of reactant molecules in the catalyst active surface would be disturbed by the precipitation problem of the given catalyst(Arita et al., 2008).

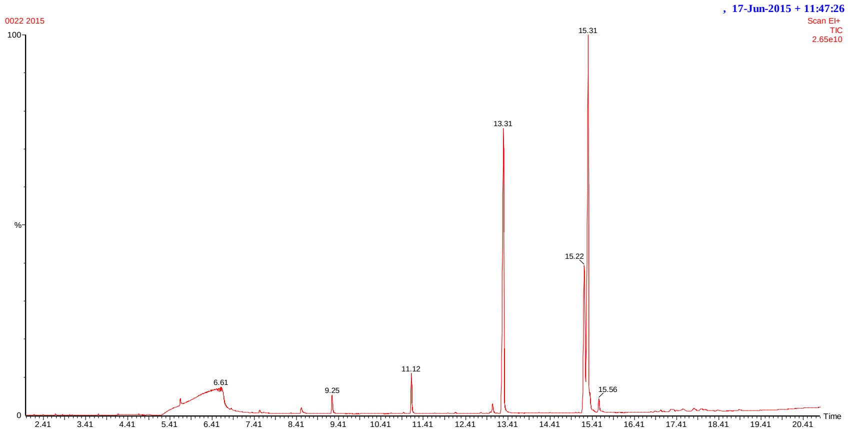

Figure 2. The Chromatogram of GCMS biodiesel synthesis product

$$CaO_{(s)} + SrO_{(s)} + 2CO_{2(g)} \rightarrow CaCO_{3(s)} + SrCO_{3(s)} \tag{4}$$

$$CaCO_{3(s)} + SrCO_3 + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + Sr(OH)_{2(s)} + 2CO_{2(g)} \tag{5}$$

The optimized result from transesterification reaction time variance and catalyst amount showed that the maximum time of transesterification reaction and the catalyst amount of CaO.SrO (1:1) was 120 minutes (2 hours) and 1%. In that optimized result, a transesterification reaction was conducted once again, to produce a biodiesel that was enough to be characterized in its biodiesel physical. In an optimum condition a pure biodiesel was produced for 24.1 mL from the volume of waste cooking oil that was used for about 25 mL. The calculation result found that the biodiesel yield percentage that was produced was 96.4% and the result of optimum condition was analyzed with GCMS to determine the metal ester fat acid components. The biodiesel chromatogram as the optimized product can be seen in Figure 2.

The chromatogram in Figure 2 showed four prior peaks in the retention time and consentration respectively was the first peak with the retention time of 11.122 minutes for 3.76 % (methyl miristat), the second peak 13.308 minutes for 39.81% (methyl palmitat), the third peak 15.224 minutes for 15.87% (methyl linoleat), and the fourth peak 15.314 minutes for 40.56% (methyl oleat). This transesterification reaction was using a solid catalyst heterogeneous base .SrO (1:1), but the expected catalyst could not be produced because the difactogram pattern as the product of XRD test showed the existence of $Ca(OH)_2$and $CaCO_3$. The fault in the making of this catalyst was analyzed with *Match!* and it proved that there were$Ca(OH)_2$dan $CaCO_3$ peaks that was more dominant than the pure CaO or SrO even CaO.SrO. Rahmawati et al. (2012) reported that the open condition of sample when it was characterized by XRD was more likely to form $Ca(OH)_2$ and $CaCO_3$in reaction with H_2O dan CO_2 from the atmosphere during the XRD analysis. The reaction scheme that was occured in the CaO.SrO catalyst which experience a spontaneous reaction with the surrounding atmosphere was shown in Eq. (4) and (5).

The error in the making of CaO.SrO (1:1) catalyst that produced $Ca(OH)_2$ did not affect the methyl ester product. Kouzu et al. (2008) had reported that $Ca(OH)_2$ could still be used as a catalyst in the transesterification reaction of soybean oil with the biodiesel yield produced reaching 93% for 3.5 hours. The test of physical characterization of biodiesel to determine the physical quality with as required in Indonesian National Standard (SNI). The data of physical characterization that was conducted included density, kinematics viscosity, biodiesel bias index as can be seen in Table 1.

Table 1 showed the value of biodiesel density for 0.851 g/mL, this value had decreased because trigliseride in the oil had converted to methyl ester that had a lower density than trigliseride (Kartika & Widyaningsih, 2012). The viscosity value of biodiesel result of the synthesis was 2.427 cSt correspond with the SNI requirement for biodiesel that is 2.3-6.0 cSt. If the fuel was too thick, it can be difficult for the current, pumping, and ignition. If the fuel was too light, it can be difficult for the distribution of the fuel so it was difficult to burn and will lead to a leak in the injection pipe (Setiawati & Edwar, 2012). The smallest index bias was biodiesel, because the speed decreased as the heating effect, so the light speed in the biodiesel was bigger which affected the value of

Table 1. The Data of Physical Characterization Test

Biodiesel Physical Characterization Test	Waste Cooking Oil treatment	Biodiesel product	Standard Source Biodiesel
Density (g/mL)	0.901	0.851	0.85-0.89 (SNI 04-7128-2006)
Viscosity (cSt)	20.424	2.427	2.3-6.0 (SNI 04-7128-2006)
Bias index	1.437	1.350	1.3-1.4(Sidjabat, 2004)

bias index become smaller (Sutiah et al., 2008). It showed the success of transesterification reaction that was conducted because the transesterification reaction changed trigliserida to methyl ester which had a density,kinematics viscosity, and bias index correspond with SNI 04-7128-2006.

CONCLUSION

Based on the finding and discussion it can be concluded that CaO.SrO (1:1) catalyst was a crystalline catalyst, with a small krystal level. The catalyst surface area was 10.217 m^2/g, which showed a synthesis between CaO modified by SrO was happening. The optimum condition happened in the reaction time of 120 minutes and the catalyst amount of 1% which produced a percentage of biodiesel yield for 96.4%. the product of transesterification reaction result that was analyzed with the GC-MS instrument was methyl meristat, methyl palmitat, methyl oleat, and methyl stearat.

SUGGESTION

A further experiment was needed with a different metal oxide catalyst, longer time variance, higher calcination temperature, further biodiesel physical characterization to determine the catalytic activity from the catalyst.

REFERENCES

Arita, S., Dara, M. B., Irawan, J. 2008. Pembuatan Metil Ester Asam Lemak dari CPO Off Grade dengan Metode Esterifikasi-Transesterifikasi. Jurnal Teknik Kimia. 2(15): 34-43.

Azmi, M. F. 2009. Transesterifikasi Heterogen antara Minyak Sawit Mentah dengan Metanol Menggunakan Katalis K_2O-CaO. Final Year Project. Medan: FMIPA Universitas Sumatera Utara. Indonesia.

Barokah, S., Widiarti, N. 2015. Aktivitas Fotokatalitik CuO/ZnO pada Reaksi Oksidasi Fenol. Indonesian Journal of Chemical Science. 4(2): 89-93.

Hambali, E., Mujdalipah, S., Tambunan, A. H., Pattiwiri, A.W., Hendroko, R. 2007. Teknologi Bioenergi. Jakarta: PT. Agromedia Pustaka.

Kanade K.G., Kale, B.B., Aiyer, R.C., Das, B.K. 2006. Effect of Solvents on The Synthesis of Nano-Size Zinc Oxide and its Properties. Materials Research Bulletin. 41: 590-600

Kartika, D., Widyaningsih, S. 2012. Konsentrasi Katalis dan Suhu Optimum pada Reaksi Esterifikasi Menggunakan Katalis Zaolit Alam Aktif (ZAH) dalam Pembuatan Biodiesel dari Minyak Jelantah. Jurnal Nature Indonesia. 14 (3): 219-226.

Ketaren, S. 2005. Pengantar Teknologi Minyak dan Lemak Pangan. Jakarta: UI-Press

Kouzu, M., Kazuno, T., Tajika, M., Sugimoto, Yamanaka, S., Hidaka, J. 2008. Calcium Oxide as a Solid Base Catalyst for Transesterification of Soybean Oil and its Application to Biodiesel Production. Fuel. 87: 2798-2806.

Liu. X., He, H., Wang, Y., Zhu, S. 2007. Transesterification of Soybean Oil to Biodiesel As A Solid Base Catalyst. Catalysis Communications. 8: 1107-1111.

Liu, X., He, H. Wang, Y., Zhu, S., Piao, X. 2008. Transesterification of Soybean Oil to Biodiesel Using CaO as a Solid Base Catalyst. Fuel. 87: 216-221.

Ngamcharussrivichai, C., Totarat, P., Bunyakiat, K. 2008. Ca and Zn Mixed Oxide as a Heterogeneous Base Catalyst For Transesterification of Palm Kernel Oil. Applied Catalysis A: General. 341: 77-85.

Rahmawati, S., Prasetyoko, D., Ediati, R. 2012. Sintesis Partikel Nano CaO dengan Metode Kopresipitasi dan Karakterisasinya. Final Year Project. Surabaya: Institut Teknologi Sepuluh Nopember Surabaya

Setiawati, E., Edwar, F. 2012. Teknologi Pengolahan Biodiesel Dari Minyak Goreng Bekas Dengan Teknik Mikrofiltrasi Dan Transesterifikasi Sebagai

Alternatif Bahan Bakar Mesin Diesel. Jurnal Riset Industri. 6(2): 117-127.

Sidjabat, O. 2004. Pengolahan Minyak Goreng Bekas Menjadi Biodiesel. Lembaran Publikasi. Jakarta: LEMIGAS.

Siswani, E.D, Kristianingrum, S., Suwardi. 2012. Sintesis dan Karakterisasi Biodiesel dari Minyak Jelantah pada Berbagai Waktu dan Suhu. Prosiding Seminar Nasional Penelitian. Yogyakarta: Universitas Negeri Yogyakarta.

Sutiah, K., Firdausi, S., Budi, W.S. 2008. Studi Kualitas Minyak Goreng Dengan Parameter Viskositas Dan Indeks Bias. Berkala Fisika. 11(2): 53-58.

Wendi, Cuaca, V., Taslim. 2015. Pengaruh Suhu Reaksi dan Jumlah Katalis pada Pembuatan Biodiesel dari Limbah Lemak Sapi dengan Menggunakan Katalis Heterogen CaO dari Kulit Telur Ayam. Jurnal Teknik Kimia USU. 1(4): 35-41.

Yoosuk, B., Krasae, P., Puttasawat, B., Udomsap, P., Viriya-empikul, N., Faungnawakij, K. 2010. Magnesia modified with strontium as a solid base catalyst for transesterification of palm olein. Chemical Engineering Journal. 162: 58-66

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.