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Preparation of Zirconia Catalyst from Zircon Sand and Its Catalytic Performance Evaluation for Biodiesel Production

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Abstract

Heterogeneous catalyst in biodiesel production was developed to overcome the disadvantages of the more well-established homogeneous catalysts. Zircon catalysts were known to have amphoteric properties, which were reported to be suitable for simultaneous esterification-transesterification process in biodiesel production. This study aims to investigate the effect of NaCl impregnated zirconia catalyst for biodiesel production through esterification-transesterification process. Wet impregnation method with varying NaCl mass (10-30% w/w) was applied to synthesize the zircon catalyst. The synthesized catalyst was analyzed for its crystallinity and surface morphology using XRD and SEM analyzers, respectively. The effect of catalyst mass (0.5-2.5% m/m) and operating temperature (50-70°C) on biodiesel product were also investigated. The biodiesel composition, density and viscosity were analyzed using GCMS analysis, picnometry and viscosimetry, respectively. The XRD and SEM results proved that the synthesized zircon catalyst with 20% m/m NaCl loading had a tetragonal structure. The density, viscosity and free fatty acid content (FFA) of the biodiesel product decreased along with increasing catalyst mass, while the fatty acid methyl ester content (FAME) increased. The increasing FAME content was attributed to the increasing number of active sites, which accelerate the esterification-transesterification reaction process, yielding more biodiesel product.

Keywords: *biodiesel; catalyst; esterification; NaCl; transesterification; zircon*

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INTRODUCTION

Indonesia's diesel oil consumption continues to increase by an average of 7% per year, with an estimated diesel oil consumption in 2020 reaching 34 million kiloliters (Sugiyono, 2006). As petroleum reserves are depleting (Marchetti *et al*., 2007), the scarcity of fuel oil is also currently happening resulting in an increased fuel oil demand that triggers a wide impact on various sectors of life. Biodiesel, an alternative fuel for diesel fuel is an attractive solution for its demand due to its abundant raw material availability, biodegradability and non-toxic properties.

In addition, it can be derived from renewable sources, that demonstrates excellent lubrication properties and high cetane number (Singh and Dipti, 2010).

Biodiesel is widely produced using homogeneous catalysts through esterification and transesterification reactions (Buasri *et al*., 2009; Theam *et al*., 2015). However, the use of homogeneous catalyst suffers from several serious weaknesses both in terms of economy and technological efficiency. Hence, heterogeneous catalysts are undergoing continuous development to overcome these disadvantages. The use of heterogeneous catalyst in biodiesel production provides the advantages, especially that are related to separation between products and unreacted raw materials as well as catalyst reuse potential (Nur *et al*., 2014). Furthermore, heterogeneous catalysts which were mostly alkaline metal oxides were less corrosive and generally demonstrate a high catalyst activity and selectivity (Gryglewicz, 1999). Heterogeneous catalysts which were commonly used in biodiesel production were CaO (Zhang *et al*., 2014), MgO (Lu *et al*., 2015), SrO (Tantirungrotechai *et al*., 2013) and $Ca(OCH_3)_2$ (Theam *et al*., 2015). These catalysts were generally only suitable for individual esterification or transesterification due to their nature, either being only acidic or basic, which were proven to be inefficient in biodiesel production. Therefore, it was imperative that a catalyst, which contains both the acidic and basic sites to be developed for enhanced biodiesel production.

Zirconia (ZrO_2) has been recognized as an interesting material due to its amphoteric and redox properties (Wang *et al*., 2000). The utilization of zirconia was only accounted for 55% of the total world production of the material, which was mainly used in the ceramic industry (Suseno, 2015). Zirconia is a grayish-white metal with a tetragonal crystalline structure (Gauna *et al*., 2015). With the abundance of the material, along with its dual acid-base reactivity ability, zirconia is a potential material for heterogeneous catalyst in biodiesel production.

Therefore, the objectives of this study are (i) to develop a heterogeneous catalyst derived from zirconia for enhanced biodiesel production (ii) to investigate the effects of NaCl impregnation in the zirconia catalyst to the biodiesel production and (iii) to evaluate the biodiesel produced from waste cooking oil (WCO) as raw material and the synthesized Na-KI/zirconia catalyst.

MATERIAL AND METHOD

Materials

Zirconia sand as the catalyst raw material was obtained from PT. Putra Dewa Bangka, Pangkalpinang, Bangka. Waste cooking oil (WCO) for the raw material of biodiesel production was obtained from local food premises in Tembalang, Semarang. Other chemical reagents used were NaCl (99.5%, Merck, Germany), KI (99.5%, Merck, Germany), methanol (99.9%, Merck, Germany), Al $(OH)_3$ (99%, Merck, Germany), NaOH (97%, Merck, Germany), phenolphthalein (Merck, Germany) and deionized water.

Variables and Control

The independent variables in this study were variation of NaCl concentration (10, 15, 20, 25, 30% *m/m*), catalyst mass loading (0.5, 1, 1.5, 2, 2.5% *m/m*) and operating temperature (50, 55, 60, 65, 70 ºC). Whereas the control variables included the esterification-transesterification operation time (4 h), stirring speed (600 rpm), methanol to WCO molar ratio of 10:1, zirconia sand size (0.42 mm) and mass (15 g), catalyst calcination temperature (650ºC) and time (5 h).

Methods

The synthesis of catalyst started with the pre-treatment of zirconia sand. The zirconia sand was sifted to a homogenous 0.42 mm size, and then washed with deionized water to eliminate the impurities, specifically the adhering dust. Next, 30 g of the washed zirconia sand was mixed with 1 M of $Al(OH)_3$ for 24 h, washed with deionized water and dried at 60 ºC overnight using vacuum oven (DZF-6020, MTI Corporation, USA).

To synthesize the NaCl/zirconia catalyst, wet impregnation method was carried out by mixing 15 g of pre-treated zirconia sand and the varying mass of NaCl, stirred at room temperature for 2 h using magnetic stirrer (MS7-H550-S, DLAB, China). The slurry mixture was then evaporated at 110ºC to remove the water content before further calcined using tube furnace (Lindberg/Blue M, Asheville, NC, USA) at 650ºC for 5 h. After calcination, the catalyst was impregnated again with 5% *m/m* KI and stirred for 2 h at room temperature. The catalyst was heated to 110 ºC before being dried in the desiccator. The synthesized NaCl/zirconia catalyst was determined its crystallinity via X-ray Diffraction (XRD) analysis and surface morphology via Scanning Electron Microscopy (SEM).

Waste cooking oil (WCO) was used as the raw material in the biodiesel production. Pre-treatment of WCO included filtration of the oil to remove food scraps. The WCO was determined for its free fatty acid (FFA) content through acid-base titration, composition via Gas Chromatography Mass Spectrometry (GCMS), density was measured using a picnometer and kinematic viscosity was evaluated using an Ostwald viscosimeter.

The performance of the synthesized catalyst was investigated through biodiesel production via esterification-transesterification reaction. First, 300 mL of WCO was placed into a three-necked round bottomed flask and heated to a pred-determined temperature. Methanol was added to the oil in methanol to oil molar ratio of 10:1, along with the synthesized NaCl/zirconia catalyst with varying mass.

The mixture was stirred at 600 rpm for 4 h. The biodiesel product was separated using a separating funnel, and later analyzed for its FFA content using acid-base titration, composition via GCMS analysis. Meanwhile, its density and kinematic viscosity were measured using picnometer and Ostwald viscosimeter, respectively.

RESULTS AND DISCUSSION

Catalyst Characterization

Figure 1 showed the XRD result of the synthesized catalyst with varying NaCl % *m/m* impregnation.

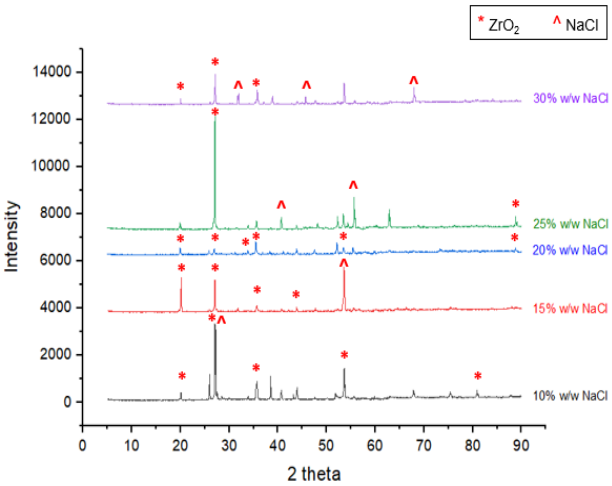

Figure 1. Diffractogram of Synthesized Catalysts

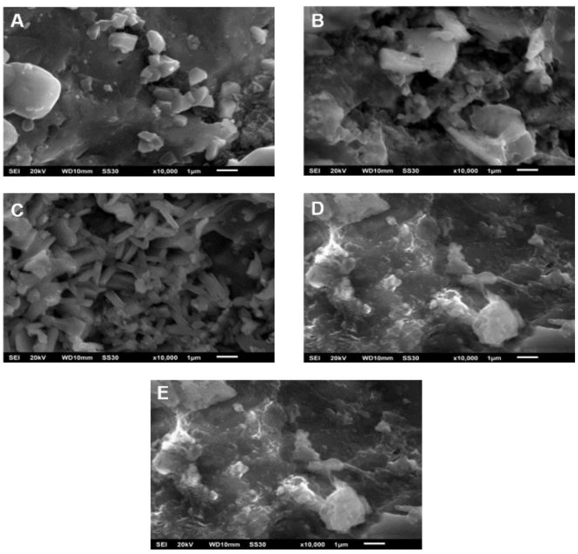

Figure 2. SEM Analysis of Synthesized Catalysts (A) 10% *m/m* NaCl, (B) 15% *m/m* NaCl, (C) 20% *m/m* NaCl, (D) 25% *m/m* NaCl and (E) 30% *m/m* NaCl

The surface morphologies of the synthesized Na-KI/Zircon catalyst were shown in Figure 2. From the results it could be inferred that the impregnation of NaCl played a role in the structure of the catalysts. As seen in Figure 2(A), when the smallest amount of NaCl was impregnated, it formed an irregular, small sized particles. As the amount of NaCl impregnation increases, the particles grew in size, forming bigger lumps of particles which observable irregular shape (Figure 2(B)). When the impregnation of NaCl was further increased to 20% *m/m*, the catalyst was shown to form a relatively same-sized tetragonal shaped particles (Figure 2(C)). This particular shape of particles was caused by ZrO_2 compound which was identified to be tetragonal in structure from the XRD results (Figure 1). Furthermore, from the SEM image it could also be seen that the structure was highly crystalline, with clearly defined shapes and order (Marhan, 2020) which further supported the conclusion of the catalyst having a crystalline structure from the XRD result, based from the strong and many ZrO_2 characteristic peaks detected (Figure 1).

Figure 2(D) and 2(E) display the synthesized Na-KI/Zircon catalyst with 25% *m/m* and 30% *m/m* impregnation giving irregular lumps of particles, which were relatively bigger in size compared to the 10% *m/m* and 15% *m/m* NaCl variation. It could also be seen that there was no regular lattice structure of particles, which meant less crystallinity. This conclusion was supported by the XRD results of the 25% *m/m* and 30% *m/m* NaCl impregnation, which only showed 2 to 3 characteristic peaks identified as ZrO_2 and also the generally small and little peaks which indicated an amorphous structure.

Crystalline structure meant an orderly arrangement of particles, with the same size and distance between each other (Marhan, 2020). The equal and neat distribution of particles would lead to a larger surface area and hence more active sites for reactions to take place (Chung *et al.*, 2020), which was one of the important qualities that a catalyst should have. Oppositely, irregular shaped agglomerates or big lumps of particles would result in a bulkier catalyst which provided less surface area available for a reaction to proceed. Therefore, it can be concluded that 20% *m/m* of NaCl was the best impregnation variable as it resulted in the most crystalline structured catalyst compared to the other impregnation variables.

Catalyst Performance in Biodiesel Production

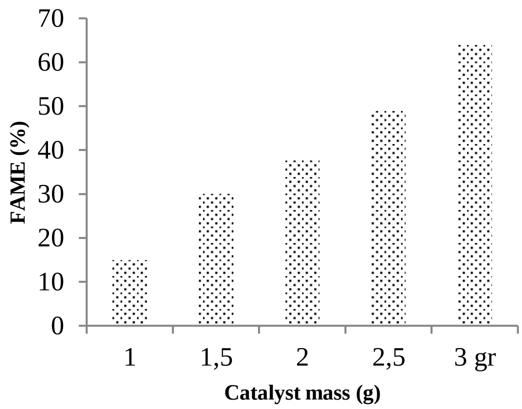

Figure 3. Effect of Catalyst Mass to % FAME in Biodiesel

The effect of catalyst mass to the biodiesel performance (% FAME) was carried out at 1:10 WCO/methanol molar ratio and 60ºC reaction temperature for 4 h with varying Na-KI/Zircon catalyst mass (1, 1.5, 2, 2.5, 3 g). The results depicted in Figure 3 showed that % FAME is directly proportional to the amount of catalyst added. The relationship is attributed to the higher mass transfer resistance present in higher catalyst loading, thereby causing larger contact area between WCO and methanol (Kusmiyati *et al.*, 2019).

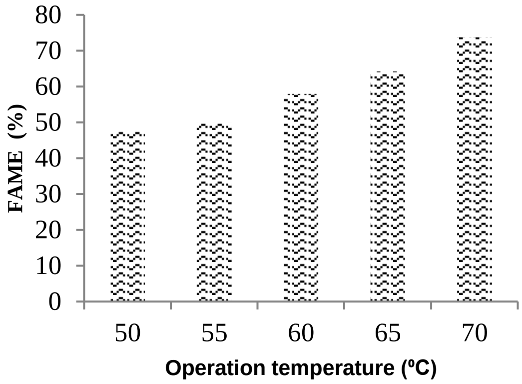

Figure 4. Effect of Operation Temperature to %FAME in Biodiesel

Meanwhile, the effect of operating temperature (50, 55, 60, 65, 70ºC) to the biodiesel performance (%FAME) was also investigated using the same reaction parameters as previously mentioned. Based on Figure 4, the %FAME was found to increase with the increase in operating temperature. Operating temperature is known to be one of the determining factors in FAME formation. Methanol dispersion speed in WCO and WCO viscosity reduction on increasing operation temperature influence the triglyceride solubility in methanol. Subsequently, it would also gradually affect the contact time between the WCO molecules and methanol, consequently affecting the FAME conversion (Chuah *et al.*, 2015).

The characteristics of biodiesel product were also analyzed in this study, namely, density, viscosity, and free fatty acid (FFA) content. Viscosity is one of the most crucial parameters in diesel engine due to its pivotal role in fuel spray, mixture formation and combustion process. High viscosity would impede the injection process and cause insufficient fuel atomization. Meanwhile, high biodiesel density would cause incomplete combustion, consequently increasing the engine wear and tear, as well as emission.

Table 1. Effect of catalyst mass to biodiesel characteristics

Parameters	Catalyst mass (g)					SNI
	1	1.5	2	2.5	3	
Density (g/cm^3)	0.900	0.898	0.893	0.886	0.881	0.85-0.90
Viscosity (cSt)	6.7	5.4	4.1	3.7	3.3	<6 at 40ºC
%FFA	2.05	1.79	1.57	1.45	1.19	<1
Cetane number	34.2	37.6	42.1	48.8	54.1	>51

Table 2. Effect of operation temperature to biodiesel characteristics

Parameters	Operation temperature (ºC)					SNI
	50	55	60	65	70	
Density (g/cm^3)	0.896	0.893	0.886	0.881	0.873	0.85-0.90
Viscosity (cSt)	4.7	4.2	3.5	3.3	2.8	Max. 6 at 40ºC
%FFA	2.70	2.20	1.45	1.19	0.90	<1
Cetane number	49.1	50.2	54.1	58.3	61	>51

These parameters were investigated to determine whether the synthesized product fulfilled the Indonesian national standard requirement (SNI) – which is important for future commercialization aspect.

Tables 1 and 2 exhibit the characterization results based on the catalyst mass and operation temperature parameters, respectively. Biodiesel products that met the national standard requirement were variables 3 g catalyst mass and 70ºC operating temperature. This finding coupled with the FAME yields of both variables (Figure 3 and 4) conclude that 3 g catalyst mass and 70ºC operating temperature is the most suitable operating conditions for biodiesel production with the synthesized Na-KI/Zircon catalyst. Another evidence of the Na-KI/Zircon catalyst good performance could be seen from its success in reducing the FFA content in biodiesel products (0.90-2.70%) from the original 5.35% in WCO. Cetane number was also directly related to the FFA content in biodiesel product. Lower FFA content would give higher cetane number as the biodiesel became easier to ignite.

CONCLUSION

The 20 *%m/m* Na-impregnated Na-KI/Zircon catalyst possesses a tetragonal crystal structure with relatively high crystallinity. Higher catalyst mass resulted in higher FAME yield due to the larger contact area between WCO and methanol caused by higher mass transfer resistance. The operation temperature and catalyst mass effects were investigated in this study. It was found that 70ºC operating temperature and 3 g catalyst mass loadinf gave the highest FAME yield.

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REFERENCES

Buasri, A., Chaiyut, N., Ketlekha, P., Mongkolwatee, W. and Boonrawd, S., (2009), Biodiesel from Crude Palm Oil with a High Content of Free Fatty Acids and Fuel Properties, *Chiang Mai University Journal of Natural Sciences*, 8(1), pp. 115-124.

Chuah, L. F., Yusup, S., Aziz, A. R. A., Bokhari, A., Klemes, J. J. and Abdullah, M. Z., (2015), Intensification of Biodiesel Synthesis from Waste Cooking Oil (Palm Olein) in A Hydrodynamic Cavitation Reactor: Effect of Operating Parameters on Methyl Ester Conversion, *Chemical Engineering and Processing: Process Intensification*, 95, pp. 235-240.

Chung, H.Y., Wu, X., Amal, R. and Ng, Y.H., (2020), Balancing the Crystallinity and Specific Surface Area of Bismuth Tungstate for Photocatalytic Water Oxidation, *Molecular Catalysts*, 487, 110887.

Gauna, M.R., Conconi, M.S., Gomez, S., Suárez, G., Aglietti, E.F. and Rendtorff, N.M., (2015), Monoclinic-Tetragonal Zirconia Quantification of Commercial Nanopowder Mixtures by XRD and DTA, *Ceramics – Silikáty*, 59 (4), pp. 318-325.

Gryglewicz, S., (1999), Rapeseed Oil Methyl Esters Preparation Using Heterogeneous Catalysts, *Bioresource Technology*, 70, pp. 249-253.

Lu, F., Wei, Y., Yu, X. and Tu, S., (2015), Transesterification of Vegetable Oil to Biodiesel over Mgo-Li_2O Catalysts Templated by a PDMS-PEO Comb-like Copolymer, *Energy Procedia*, 75, pp. 72-77.

Marchetti, J.M., Miguel, V.U. and Errazu, A.F., (2007), Possible Methods for Biodiesel Production, *Renewable and Sustainable Energy Reviews*, 11, pp. 1300-1311.

Marhan, G.D., (2020), Crystal, *Encyclopaedia Britannica*, accessed on 02 December 2020 at www.britannica.com/science/crystal.

Shajaratun Nur, Z.A., Taufiq-Yap, Y.H., Rabiah Nizah, M.F., Teo, S.H., Syazwani, O.N. and Islam, A., (2014), Production of Biodiesel from Palm Oil Using Modified Malaysian Natural Dolomites, *Energy Conversion and Management*, 78, pp. 738-744.

Singh, S.P. and Dipti, S., (2010), Biodiesel Production Through the Use of Different Sources and Characterization of Oils and Their Esters as the Substitute of Diesel, *Renewable and Sustainable Energy Reviews*, 14, pp. 200-216.

Sugiyono, A., (2006), Peluang Pemanfaatan Biodiesel dari Kelapa Sawit sebagai Bahan Bakar Alternatif Pengganti Minyak Solar di Indonesia, *Badan Pengkajian dan Penerapan Teknologi*.

Suseno, T., (2015), Analisi Prospek Pasir Zirkon Indonesia di Pasar Dunia, *Jurnal Teknologi Mineral dan Batubara*, 11(1), pp. 61-77.

Tantirungrotechai, J., Thepwatee, S. and Yoosuk, B., (2013), Biodiesel Synthesis over Sr/MgO Solid Base Catalyst, *Fuel*, 106, pp. 279-284.

Theam, K.L., Islam, A., Choo, Y.M. and Taufiq-Yap, Y.H., (2015), Biodiesel from Low-Cost Palm Stearin Using Metal Doped Methoxide Solid Catalyst, *Industrial Crops and Products*, 76, pp. 281-289.

Wang, Y., Huang, W.Y., Wu, Z., Chun, Y. and Zhu, J.H., (2000), Superbase Derived from Zirconia-Supported Potassium Nitrate, *Materials Letters*, 46(4), pp. 198-204.

Kusmiyati, K., Prasetyoko, D., Murwani, S., Fadhilah, M. N., Oetami, T. P., Hadiyanto, H., Widayat, W., Budiman, A. and Roesyadi, A., (2019), Biodiesel Production from *Reutealis Trisperma* Oil Using KOH Impregnated Eggshell as A Heterogeneous Catalyst, *Energies*, 12(19), 3714.

Zhang, P., Han, Q., Fan, M. and Jiang, P., (2014), Magnetic Solid Base Catalyst CaO/$CoFe_2O_4$ for Biodiesel Production: Influence of Basicity and Wettability of the Catalyst in Catalytic Performance, *Applied Surface Science*, 317, pp. 1125-1130.