

COMPARATIVE PERFORMANCE OF SiO_2/CaO SUPERBASE AND SULFATED- TiO_2/ZnO SUPERACID NANOCOMPOSITE CATALYSTS FOR SINGLE-STEP SYNTHESIS OF GREEN-DIESEL

I. N. Simpen¹, I.N.S. Winaya^{2,✉}, I.D.G.A. Subagia³ and I.W.B. Suyasa⁴

^{1,4}Chemistry Study Program, Faculty of Mathematics and Natural Sciences, Udayana University, Bali 80361, Indonesia

^{2,3}Mechanical Engineering Study Program, Faculty of Engineering, Udayana University, Bali 80361, Indonesia

✉Corresponding Author: ins.winaya@unud.ac.id

ABSTRACT

Bio-diesel or green-diesel consists of a long chain mixture of FAMES (fatty acid methyl esters). It can be produced when a major component of triglycerides and free fatty acids (FFAs) reacts with methanol and using a catalyst. The catalyst increased the reaction rate to produce green diesel. This study aims to compare the performance of SiO_2/CaO superbase and sulfated- TiO_2/ZnO superacid nanocomposite catalysts for single-step synthesis of green diesel in esterification-transesterification reactions. The SiO_2/CaO superbase was prepared by mixing SiO_2 and CaO using sol-gel methods and the sulfated- TiO_2/ZnO superacid by impregnation of sulfuric acid on TiO_2 powder and ZnO powder, then mixed by physical mixing-calcination methods. Synthesis of green diesel was carried out by converting used cooking palm oil (UCPO) in the single-step process. Results have shown that the performance of the SiO_2/CaO catalyst was relatively higher than the sulfated- TiO_2/ZnO catalyst, with a conversion efficiency of green diesel of 86.14% and 83.65%, respectively. However, the performance of the sulfated- TiO_2/ZnO catalyst in reducing FFAs was relatively higher than SiO_2/CaO catalyst. The catalyst's characteristics, namely surface area, basicity-acidity, and active sites exposed on the surface were determinants of the conversion efficiency of green diesel. Mean crystallite size distribution and surface morphology correlated with surface area and performance of the catalysts. The main conclusion is that the superbase and the superacid solid catalysts can be considered for their activity to convert UCPO into green diesel in a single-step process.

Keywords: Esterification-Transesterification, Green-Diesel, Single-Step Process, SiO_2/CaO Superbase, Sulfated- TiO_2/ZnO Superacid.

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INTRODUCTION

Green diesel (biodiesel) can be synthesized by methods of blending and direct use, microemulsions, thermal cracking, and transesterification. Of these methods, transesterification is famous because it is relatively easier to be done under normal conditions, provides high conversion efficiency, and has the best quality compared to other methods.^{1,2} In the transesterification and/or esterification methods, green diesel is synthesized by mixing oil and a short chain of alcohol (methanol) using a catalyst.^{3,4} Heterogeneous (solid) catalysts can overcome the disadvantages of homogeneous (liquid) catalysts.^{5,6} Solid catalysts have the advantage of properties, which are easily separated from biodiesel products, do not form foam due to neutralization of FFAs and triglycerides saponification^{7,8,9} as well as non-toxic, non-corrosive, and can also be regenerated so that it can be reused.¹⁰ In addition, the esterification and the transesterification reactions can be done simultaneously (in a single-step process).^{7,11,12} Biodiesel synthesis in the esterification method from used cooking oil through utilization of the solid acid catalysts was carried out using $\text{SO}_4/\text{Fe-Al-TiO}_2$ ¹³, S- TiO_2/SBA (Santa Barbara amorphous)-15¹⁴ and sulfated TiO_2 .^{15,16} Meanwhile, solid base catalysts of CaO from clamshells¹², CaO from eggshells¹⁷, CaO in dolomite¹⁸ and pure CaO ^{19,20} have been used in the transesterification method. However, the weakness of high CaO content is that it hydrates quickly, when mixed with methanol it easily forms a paste and carbonates at room temperature, making the catalyst function less stable. As a result, less oil is being turned into biodiesel.^{4,21} The CaO can be combined to

overcome its weakness with SiO_2 , which is more stable in the property. The SiO_2 has a weak surface basicity but a large surface area, pore volume, and good stability.²² These studies utilize limited solid catalysts for esterification and transesterification methods separately, not yet simultaneously, and even combined with liquid catalysts. Thus, it is necessary to study the utilization of superbase and superacid solid catalysts in a single-step process of esterification and transesterification. On the other hand, to increase the selectivity of the sulfated- TiO_2 catalyst for the synthesis of green diesel from UCPO in the single-step process, the sulfated- TiO_2 is combined with sulfated- ZnO to obtain sulfated- TiO_2/ZnO superacid nanocomposite. Liu and Zhang (2011) studied different morphologies and weak acidity of the ZnO material that the ZnO granular catalyst was able to produce biodiesel in esterification with a yield of 46.2% compared to nano ZnO powder (73.5%).²³ The nanocomposite catalyst materials with relatively high surface-active sites concentration and large surface area to volume ratios must be achieved, to its effectiveness in biodiesel production. Therefore, the performance of both superbase and superacid nanocomposite catalysts in the synthesis of green diesel in the single-step process is important to study and it is different from previous studies. The primary goal of this study is to utilize solid catalysts of SiO_2/CaO superbase and sulfated- TiO_2/ZnO superacid nanocomposites for green-diesel synthesis from used cooking palm oil (UCPO) in the single-step of esterification-transesterification. The study also investigates its comparative characteristics and performance to the conversion efficiency of green diesel.

EXPERIMENTAL

Materials

In these experiments, the materials that were used rice hush ash as a source of green-silica (SiO_2 of 92.10%) collected from rice hush waste in Gianyar-Bali as well as chicken eggshell as a source of green-calcium oxide (CaO of 99.25%) and UCPO (FFAs content of 3.05%) collected from household waste in Gianyar-Bali. Chemicals included Titania (TiO_2) (purity: 98%), zinc oxide (ZnO) (purity: 95.53%), sulfuric acid (purity: 95-97%), ethylene glycol (purity: 99%) and methanol (purity: 99.9%).

The Synthesis of SiO_2/CaO Superbase Nanocomposite Catalyst

The SiO_2/CaO composite was synthesized by using the sol-gel methods. Eighteen (18.0) g of a mixture of SiO_2 and CaO powder (mass ratio 55% and 45%, respectively) were added to 100 mL of ethylene glycol with vigorous stirring and heated at 60°C in a reflux apparatus for 4.5 h until became sol. After the sol was formed, added by dropwise of 2.5 M NaOH solution to 50 mL into a gel formed and allowed to stand for 30 min. The gel was washed repeatedly until free from the remaining NaOH solution with distilled water. Then, dried it at $105\text{--}110^\circ\text{C}$ for 4 h and calcinated at 500°C for 1.5 h. The obtained SiO_2/CaO composite was crushed and sieved in size 100-200 mesh.

The Synthesis of Sulfated- TiO_2/ZnO Superacid Nanocomposite Catalyst

(1) The sulfated TiO_2 was prepared by mixing 10.0 g of TiO_2 powder with 200 mL of 2.5 M sulfuric acid solution and stirring for 24 h at medium speed. Afterward, the obtained sulfated- TiO_2 was filtered by Whatman 1 filter paper and washed until free sulfate ions. It was then calcinated for 4 h at 500°C .^{11,24,25} (2) The sulfated ZnO was prepared by mixing 10.0 g of ZnO powder with 200 mL of a solution of 0.5 M sulfuric acid for 24 h at medium speed. Furthermore, the obtained sulfated- ZnO was washed and filtered with Whatman 1 filter paper until free sulfate ions. It was then calcinated for 4 h at 500°C . (3) Sulfated- TiO_2/ZnO composite was synthesized through the physical mixing-calcination methods. The sulfated- TiO_2 was blended equitably with sulfated- ZnO in a dish of porcelain with a mass proportion of 1:1 and ethanol added at the proportion of 1:2, then calcinated at 550°C for 3 h.

Characterization of Nanocomposite Catalysts

The obtained composites were characterized namely surface basicity-acidity by base-acid titrations (ASTM D664) and ammonia sorption (ASTM D4824-13) methods, sulfur (S) element by using an ultimate analyzer of Leco Elementary S Type 628S (ASTM D4239), BET specific surface area and BJH porosity by using a surface area analyzer of Qunatachrome Novatouch LX-4 (ASTM 3663-20), crystallinity by using X'pert pro analytical XRD (ASTM D3956-19), surface morphology by using JEOL JSM-6510 LA SEM (ASTM E1508-12a) and TEM of JEOL JEM 1400 (ASTM E3143-18b).

Performance Test of Catalyst into Green-Diesel Synthesis in Esterification-Transesterification Single-Step Process

The UCPO was filtered to rid of any impurities, then evaporated for 30 min at 105-110°C. Additionally, SiO₂/CaO and sulfated-TiO₂/ZnO composites were used as catalysts for a single-step synthesis of green diesel in esterification-transesterification at 3% catalyst concentrations to oil; 6:1 mole ratios of methanol/oil and 60-min reaction times. At 60°C and a moderate mixing intensity, all processes are carried out. The mass yield of synthesized green-diesel is expressed as a percentage of $\frac{\text{amount of synthesized green-diesel}}{\text{amount of oil}} \times 100$.^{26,27} The green-diesel chemical compositions (FAMEs content percent) are analyzed by using GC-MS of Shimadzu QP2010 SE (ASTM E2997-16). The conversion efficiency percent and FFAs reduction percent are calculated as $(\text{mass yield percent} \times \text{FAMEs content percent}) \times 100$ and $\frac{\text{FFAs of oil} - \text{FFAs of synthesized green-diesel}}{\text{FFAs of oil}} \times 100$, respectively.²⁶

RESULTS AND DISCUSSION

Catalyst Characteristics

Surface Basicity-Acidity, Active Sites Number, and Sulfur (S) Element

The surface basicity of the SiO₂/CaO composite catalyst was classified as very high and in line with the base site's number so it is included in the superbase category (Table-1). Meanwhile, the sulfated-TiO₂/ZnO composite catalyst had high surface acidity and was in line with the acid site number and S elements, so it is classified as superacid. The superbase and superacid catalysts provided reactivity of each for their performance in green-diesel synthesis. It is important to take how into account when applying the acid-base concept to solid surfaces. From a specific structure of active sites, the functions are derived.^{28,29}

Table-1: The Surface Basicity-Acidity, the Base-Acid Sites Number, and the S Element of Catalysts

Catalyst type	Surface basicity (mmole of HCl/g)	Base sites number (x10 ²⁰ sites/g)	Surface acidity (mmole of NH ₃ /g)	Acid sites number (x10 ²⁰ sites/g)	S element (mmole/g)
SiO ₂ /CaO composite	22.6145	136.2071	-	-	0.0656
Sulfated-TiO ₂ /ZnO composite	-	-	8.6308	51.9833	1.2932

Surface Area and Porosity

Based on data in Table-2, the BET-specific surface area and the porosity (the average pore diameter and the total pore volume) of the SiO₂/CaO composite were larger than the sulfated-TiO₂/ZnO composite. The catalytic performance of a solid catalyst can be dependent on physical and chemical properties such as surface area, porosity, and the number of active sites exposed on its surface.³

Table-2: The Surface Area and Porosity of Catalysts

Catalyst type	BET-specific surface area (m ² /g)	Average pore diameter (nm)	Total pore volume (cm ³ /g)
SiO ₂ /CaO composite	10.6323	7.9348	0.0211
Sulfated-TiO ₂ /ZnO composite	7.4675	6.5610	0.0122

Crystallinity and Crystallite Size

The XRD patterns of SiO₂ were at 2θ of 21.66° and 35.84° as well as CaO at 2θ of 29.30°; 35.84°; 33.99° and 17.78° (Fig.-1a). The XRD patterns at 2θ of 36.28°; 36.18° and 31.76° for high intensity of ZnO as well as at 2θ of 25.29°; 40.01° and 37.73° for high intensity of TiO₂ (Fig.1-b). The XRD patterns were classified as dominant crystalline and minimal semicrystalline.

Scherrer formulation of $D = \frac{k\lambda}{\beta \cos \theta}$ is used to calculate catalyst crystallite sizes.^{30,31} Where D is the average crystallite size in nanometers, k is the Scherrer's constant (equivalent to 0.9), FWHM (full width at half

maximum) intensity in radians, the wavelength (λ) of the XRD source with 1.5406 Å CuK α -radiation and the diffraction angle (θ , °).

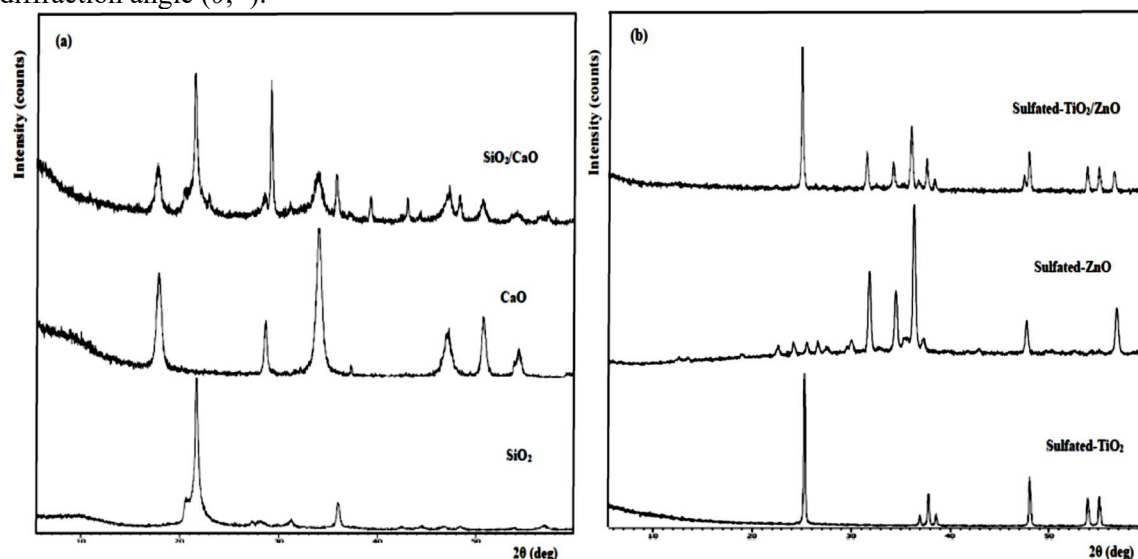


Fig.-1: XRD Patterns of (a) SiO₂/CaO Composite and (b) Sulfated-TiO₂/ZnO Composite

Table-3: The Mean Crystallite Size of Catalysts

Catalyst type	Crystallite size at 100% intensity (nm)	Mean crystallite size distribution (nm)
SiO ₂ /CaO composite	40.32	48.73
Sulfated-TiO ₂ /ZnO composite	44.27	62.55

The mean crystallite size distribution of the SiO₂/CaO composite was smaller than the sulfated-TiO₂/ZnO composite. Both composites were classified as a nanoscale (range 1-100 nm).³²

Surface Morphology

The SEM and TEM images of SiO₂/CaO and sulfated-TiO₂/ZnO composites are shown in Fig.-1 and Fig.-2, respectively. They reveal irregularly sized nanocomposite particles with a strong propensity to agglomerate.^{33,34} The SEM and TEM images were aligned to crystalline size, with the particle size of SiO₂/CaO (48.73 nm) smaller than sulfated-TiO₂/ZnO (62.55 nm) (Table-3). The particle size affected the external surface area and performance of the catalysts.³⁵

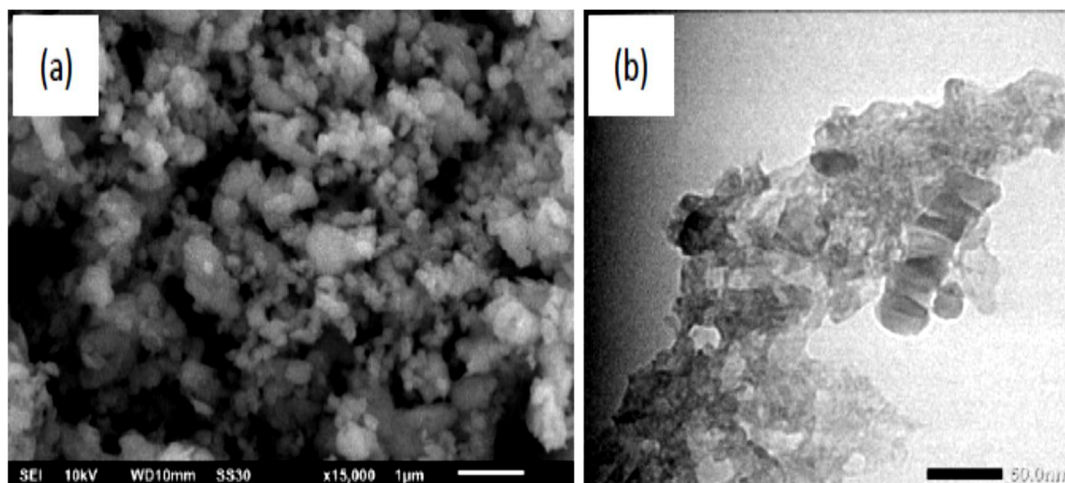


Fig.-1: The SEM Image 1μm (a) and the TEM Image 50 nm (b) of SiO₂/CaO Composite

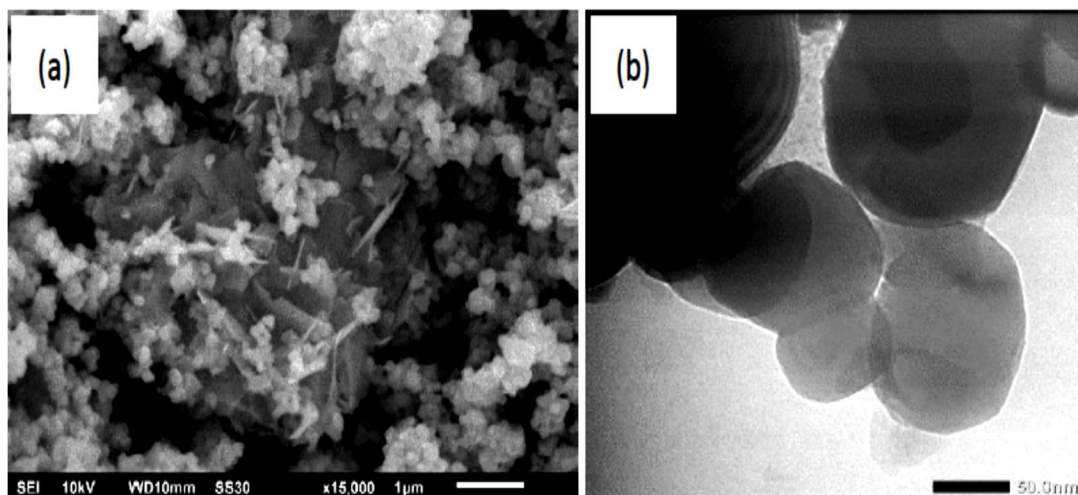


Fig.-2: The SEM Image 1 μ m (a) and the TEM Image 50 nm (b) of Sulfated-TiO₂/ZnO Composite

Green-diesel Characteristics

Conversion Efficiency and FFAs Reduction

The conversion efficiency of green-diesel using SiO₂/CaO composite catalyst was obtained relatively higher than sulfated-TiO₂/ZnO composite catalyst as shown in Table-4. The high conversion efficiency of green diesel is due to the surface basicity content which correlates with the base site number (Table-1) and their specific surface area (Table-2). The conversion efficiency of green diesel can be dependent on several factors such as surface area, porosity, and active site number in the structure of the catalyst. The structure of active sites in a solid catalyst consists of Lewis acid sites as acceptors of electrons and negative ions of oxygen (anions), including Bronsted base sites and Lewis base sites as proton acceptors.³ Meanwhile, the ability of sulfated-TiO₂/ZnO catalyst in the synthesis of green-diesel by transesterification can occur even though the catalyst has Lewis base sites and Lewis acid sites, as well as functionalizing sulfonic groups, can increase Bronsted acid sites.²⁹

Table-4: Mass Yield, FAMES Content, Conversion Efficiency, and FFAs Reduction of Green-Diesel

Catalyst type	Mass yield (%)	FAMES content (%)	Conversion efficiency (%)	FFAs reduction (%)
SiO ₂ /CaO composite	87.74	98.18	86.14	80.04
Sulfated-TiO ₂ /ZnO composite	85.08	98.32	83.65	86.34

During the methanolysis of oils, it provides enough adsorptive sites for methanol, where the O-H bonds easily break hydrogen cations and anions of methoxide. Molecules of triglyceride in oil then react with the anions of methoxide to produce FAMES.³ The reduction of FFAs was higher using sulfated-TiO₂/ZnO composite catalyst compared to SiO₂/CaO composite catalyst. The high reduction of FFAs occurred when using a sulfated-TiO₂/ZnO composite catalyst due to the high surface acidity compared to using a SiO₂/CaO composite (Table-1). This phenomenon was supported by the result obtained by Ore *et al.* (2020), that the increase of FFAs reduction was achieved in conditions of optimum contact time and then back down.³⁶ Meanwhile, the ability of SiO₂/CaO catalyst in the synthesis of green-diesel by esterification of FFAs content can occur even though the catalyst has Lewis acid sites and Lewis base sites.

Chemical Compositions

Based on Fig.-3(a), the MS analysis of chemical compositions of green-diesel with the presence of SiO₂/CaO catalyst was methyl oleate (51.08%) at retention time (Rt) 17.57 min, methyl palmitate (37.64%) at Rt 15.7 min, methyl stearate (7.34%) at Rt 17.67 min, methyl myristate (1.24%) at Rt 13.28 min, methyl palmitoleate (0.55%) at Rt 15.3 min and methyl laurate (0.33%) at Rt 10.83 min. The MS analysis of chemical compositions of green-diesel with the presence of sulfated-TiO₂/ZnO catalyst (Fig.-3(b)) were methyl oleate (50.68%) at Rt 17.58 min, methyl palmitate (37.57%) at Rt 15.72 min, methyl stearate

(7.76%) at Rt 17.68 min, methyl myristate (1.35%) at Rt 13.28 min, methyl palmitoleate (0.60%) at Rt 15.3 min and methyl laurate (0.36%) at Rt 10.83 min.

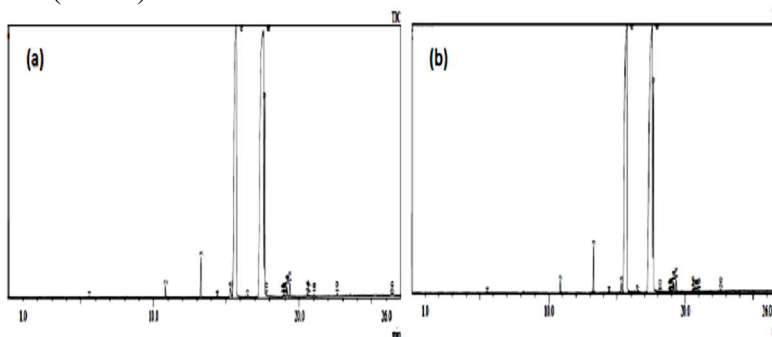


Fig.-3: The GC Chromatogram of Green-Diesel with the Presence of (a) SiO_2/CaO and (b) Sulfated- TiO_2/ZnO Composites Catalysts

Converting UCPO in a single-step process of esterification-transesterification involving both superbase and superacid catalysts was converted into FAMES >98% with dominant methyl oleate (>50%), methyl palmitate (>37%) and methyl stearate (>7%). Additionally, it is noted that methyl oleate which is present in oleic acid as the dominant component of palm oil, is the biodiesel component with the highest percentage.

CONCLUSION

The performance of the SiO_2/CaO superbase catalyst for green-diesel synthesis was mass yield of 87.74%, FAMES content of 98.18%, and conversion efficiency of 86.14%. Whereas, the performance of the sulfated- TiO_2/ZnO superacid catalyst was green-diesel mass yield of 85.04%, FAMES content of 98.32%, and conversion efficiency of 83.65%. The conversion efficiency ability of the SiO_2/CaO superbase catalyst was relatively higher than the sulfated- TiO_2/ZnO superacid catalyst. With the ability to reduce FFAs, the performance of the superacid composite catalyst was relatively higher (86.34%) than the superbase catalyst composite (80.04%). The catalysts for the one-step conversion of UCPO into green-diesel, SiO_2/CaO , and sulfated- TiO_2/ZnO nanocomposites demonstrated good catalytic performance and can be considered an application on a large scale.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest in this manuscript.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

I. N. Simpen  <http://orcid.org/0000-0003-1296-1215>

I.N.S. Winaya  <http://orcid.org/0000-0001-7920-0774>

I.D.G.A. Subagia  <http://orcid.org/0000-0001-8396-4400>

I.W.B. Suyasa  <http://orcid.org/0000-0003-3201-3685>

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