Catalytic Cracking of Crude Biodiesel Into Biohydrocarbon Using Natural Zeolite Supported Nickel Oxide Catalyst

Isalmi Aziz[a*], Edra Aditya Fhilipia Ardine[a], Nanda Saridewi[b], Lisa Adhani[c]

[a] Department of Chemistry, Faculty of Sciences and Technology, Syarif Hidayatullah State Islamic University, South Tangerang, Indonesia
[b]Department of Chemistry Education, FITK, Syarif Hidayatullah State Islamic University, South Tangerang Selatan, Indonesia
[c]Department of Chemical Engineering, Faculty of Technic, Universitas Bhayangkara Jakarta Raya, Jakarta Selatan, Indonesia

Corresponding author: isalmikimia@uinjkt.ac.id

Abstract. Crude biodiesel is biodiesel that still contained impurities. The quality can be improved into biohydrocarbons (biogasoline, biokerosene and green diesel) through catalytic cracking process. The catalyst used is nickel oxide supported natural zeolite (NiO/Zeolite). The use of nickel can increase the activity of the catalyst because it has an empty d orbital and a smaller molecular size. This study aims to determine the best catalyst that able to exhibit the greatest selectivity toward biohydrocarbons. Natural zeolite was activated and impregnated by varying the concentration of NiO (1, 3 and 5%). The characteristics of the catalyst were determined by characterized the crystallinity (X-Ray Diffraction), surface area (Surface Area Analyzer) and functional group (Fourier Transform Infra Red). The catalyst and crude biodiesel were put in an autoclave reactor and operated at a temperature of 375°C and a time of 3 hours. The obtained product was tested with Gas Cromatography Mass Spectroscopy. The results of XRD analysis showed the presence of NiO at 2θ 37.23; 43.15; and 62.65°. Nickel oxide on the catalyst was detected at a wave number of 671.23 cm^{-1}. The highest surface area was obtained at a NiO/Zeolite 1% of 49.4 m^2/g. NiO/Zeolite 1% catalysts gave the best results on catalytic cracking of crude biodiesel with a reaction conversion of 60.79% and selectivity of biogasoline 9,73%; biokerosene 29,64% and green diesel 9,18%.

Keywords: Crude biodiesel; biohydrocarbon; biogasoline; natural zeolite; nickel oxide

1. Introduction.

Crude biodiesel is produced from the oil transesterification with alcohol which is not being purified. The component of the crude biodiesel can contain byproduct, the excess of the reactant and the catalyst [1]. The conversion of the crude biodiesel generated biohydrocarbon. Biohydrocarbon is one of the biofuels which contained only hydrogen and carbon. Biohydrocarbon consists of biogasoline, biokerosene, and green diesel. The conversion of crude biodiesel into biohydrocarbon can be conducted by utilizing catalytic cracking. The catalytic cracking is more effective than the other process such as thermal cracking and hydrocracking because the catalytic cracking can be conducted at a lower temperature and exhibited cleaner process to generate the product [2].

The catalytic cracking will need a catalyst. There are many catalysts that have been used for catalytic cracking, one of them is zeolite [3]. Both natural and synthetic zeolite exhibited Brønsted and Lewis acidity which is important for the cracking process. Natural zeolite produces lower costs since the price is cheaper. To increasing the catalytic activity, the catalyst can be impregnated by using transition metals such as Co, Mo, Ni, Cu, Zn, Fe and Cr [4, 5, 6, 7]. Aziz et al., [1] upgraded the crude biodiesel by using H-Zeolite and generated 6.26% and 17.6% of gasoline and kerosene, respectively. Juwono et al., [8] achieved 91.93% of hydrocarbon ranging from C_7-C_{20} by using Pd/Al-MCM-41 as the catalyst for hydrocracking of the fatty acid methyl ester (biodiesel). Norvia et al., [9] used natural zeolite as the catalyst for biodiesel synthesis from waste cooking oil which generated 63.21% methyl ester.

To increase the catalytic activity, the natural zeolite is impregnated by using nickel oxide. Nickel oxide has been chosen because of the smaller size hence able to distribute well at the surface and the pores of the zeolite [10]. Nickel impregnation can increase the acidity of the catalyst [11]. The concentration of NiO which impregnated may vary from 1%, 3% and 5%. The catalyst obtained from the synthesis then characterized by using XRD, SAA, and FTIR to determine the crystallinity, the surface area, and the functional groups, respectively. Furthermore, the catalyst and crude biodiesel will react in the autoclave in 3 hours at 375 °C. The product obtained further determined by using GCMS.

2. Methodology.

2.1. Materials.

The experiments were carried out using Pyrex and autoclave with severalmaterials such as $Ni(NO_3)_2.6H_2O$ (Merck, 99.99%), $AgNO_3$ (Merck, 99.99%), NH_4Cl (Merck, 99.99%), distilled water, 70% ethanol, and natural zeolite (CV. Minatama Lampung).

2.2. Synthesis and Characterization of NiO/Zeolite

Natural zeolite which had purified by using distilled water was added to the reflux and NH_4Cl (1 M) was added. The reflux conducted in 3 hours at 90 °C. After reflux, the zeolite then filtered and washed until the neutral pH is reached. The calcination then carried out at450 °C until the activated zeolite (H-Zeolite) is obtained [12]. Wet impregnation then was conducted using $Ni(NO_3)_2.6H_2O$ with various concentrations e.g. 1%, 3% and 5%. The mixture was left for 6 hours then further dried in the oven. Impregnated zeolite then calcined at 500 °C to obtain the NiO/Zeolite.

The surface area is determined by using Tristar II Micromeritics SAA. The catalysts were loaded into a tube and further degassed with the N_2 at 200 KPa in 2 hours at 200 °C. The crystallinity is obtained by using Rigaku MiniFlex 600 XRD at 40 kV, 25 mA at 5-90°. The functional groups of the catalyst are achieved by using the Shimadzu FTIR spectrometer. The sample is ground with the KBr with the ratio of 1:10 and determined with the wavenumber ranging from 400–4000 cm^{-1}.

2.3. Catalytic Cracking of Crude Biodiesel

The reactor which contained crude biodiesel and catalyst then heated until 375 °C. The reaction was carried out for 3 hours [1]. The product obtained from the reaction was removed from the reactor and the composition was determined using GCMS. The sample injected through the column (DB5-MS UI stationary phase with the specification of 30 m, 0.25 mm and 0.25 µm with He mobile phase). From the area obtained in the chromatogram, the conversion and the selectivity of the product for each catalyst used in catalytic cracking using equation (1) and (2) [13].

$$\% C = \frac{\% I\quad A\quad -\% F\quad A}{\% Ii\quad A} x100\% \quad (1)$$

$$\% S = \frac{\% P\quad a}{\% T\quad p\quad a} x100\% \quad (2)$$

3. Results and Discussion

3.1. Catalyst Characterizations

The diffraction pattern of the activated natural zeolite (H-Zeolite) can be seen in Figure 1. The type of zeolite used was clinoptilolite that can be observed from the diffraction pattern obtained at 2θ of 9.84, 22.38, 22.72 and 29.94° (JCPDS No. 71-1425) with Miller indices (020), (131), (421) and (331), respectively. [14] mentioned that the peak at 2 θ of 22.39° was a special feature of clinoptilolite from Lampung. Fatimah and Utami [15]also obtained a similar 2θ of 22.25° for natural zeolite.

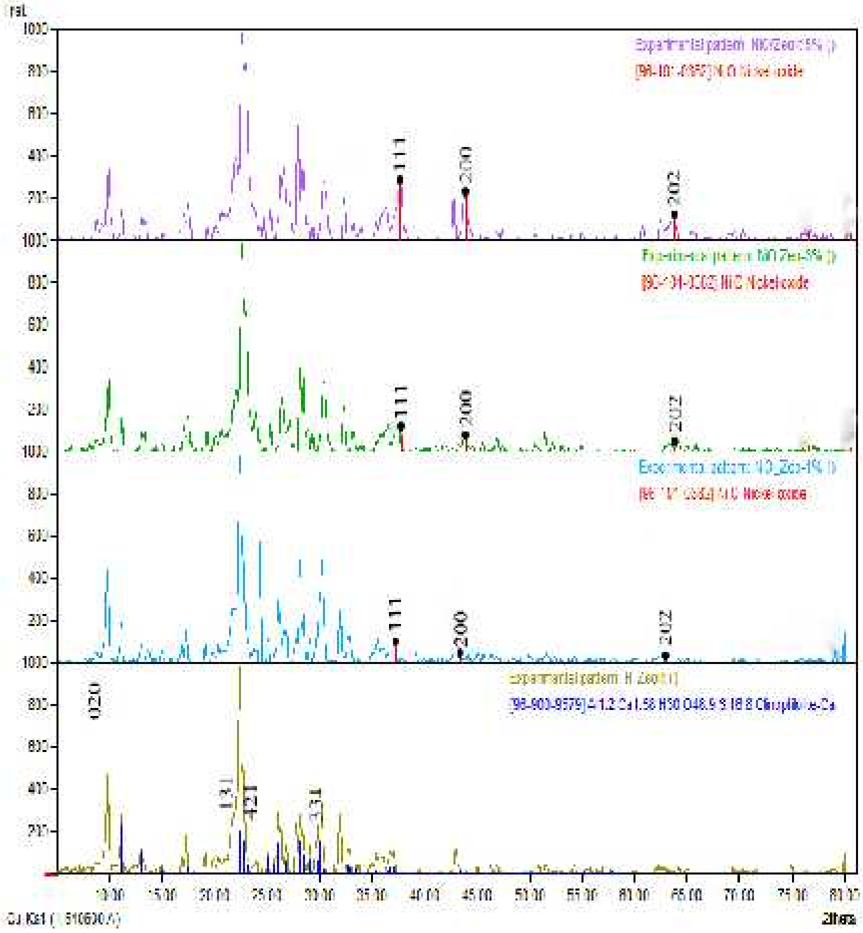


Figure 1. Diffraction patterns of H-Zeolite and NiO/Zeolite

From Figure 1, the nickel oxide impregnation did not change the diffraction pattern of the NiO/Zeolite. The presence of the nickel oxide at the catalyst can be identified at 2θ of 37.2, 43,27 and 62.87° (JCPDS No. 47-1049) with hkl: (111), (200) and (220), respectively. The concentration variation of nickel oxide which impregnated led to the different intensity as can be seen in Table 1. The larger NiO concentration results in larger intensity.

Table 1. Peak intensity of NiO at NiO/Zeolite

NiO/Zeolite (1%)		NiO/Zeolite (3%)		NiO/Zeolite (5%)		hkl
2θ	Intensity	2θ	Intensity	2θ	Intensity	
37.00	59.7	37.32	72.6	37.23	173.4	111
43.29	76.9	43.12	93.4	43.15	223.1	200
62.38	39.4	63.05	47.9	62.85	114.4	202

FTIR spectrum from H-Zeolite and NiO/Zeolite can be seen in Figure 2. Catalysts obtained had a double ring at 600–550 cm^{-1} wavenumbers which indicated the special feature of the zeolite [16]. At wavenumbers of 900–1000 cm^{-1}, the Si-O asymmetric stretching is present. Brønsted acid sites are present at 1627-1629 cm^{-1} wavenumbers to all the catalysts, but the presence of Lewis acid sites is only found for H-Zeolite at 1431.18 cm^{-1}. According to [17], Lewis acid sites and Brønsted acid sites are present at 1442–1419 cm^{-1} and 1650–1620 cm^{-1}, respectively. Kadarwati et al., [18] also obtained the Brønsted acid sites and Lewis acid sites at 1650–1620 cm^{-1}and 1401.25 cm^{-1}, respectively for the natural zeoliteused for the bio-oil pyrolysis. Nickel oxide catalyst is found at 671.23 cm^{-1} wavenumbers, whereas the peak for the H-Zeolite is not present. Rahmani et al., [19] mentioned that the metal impregnation toward zeolite results in a shift of the absorption band which not too big.

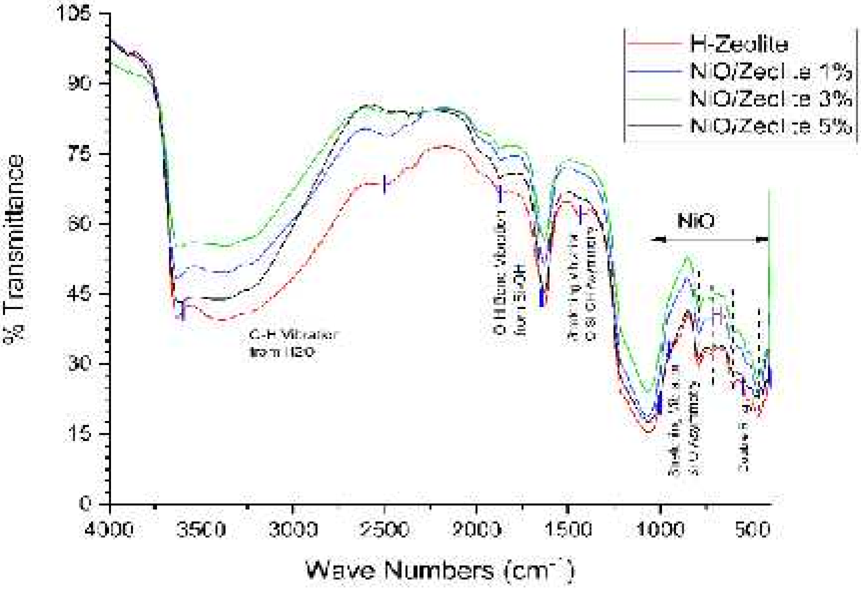


Figure 2. FTIR spectrum of H-Zeolite and NiO/Zeolite 1%, 3% and 5%

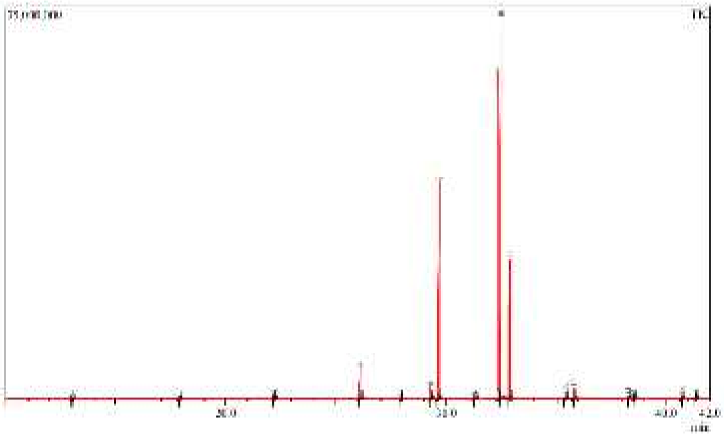
Tabel 2 showed the surface area of the H-Zeolite and NiO/Zeolite. NiO/Zeolite 1% exhibited a high surface area which is 49.410 m^2 g^{-1}. Higher surface area can increase the catalytic activity because it elevates the contact frequent between the reactant and the catalyst. Increment of NiO concentration exhibited lower surface area, which occurred due to the agglomeration and pore filled by NiO at the surface of the catalyst [20]. Ni impregnation at the HZSM-5 also decreasing the surface of the catalyst from 424.6482 to 287.3484 m^2 g^{-1} [21].

Table 2. Surface area of catalysts

Catalyst	Surface area ($m^2\ g^{-1}$)
H-Zeolite	46.166
NiO/Zeolite 1%	49.41
NiO/Zeolite 1%	39.333
NiO/Zeolite 1%	38.509

3.2. Catalytic Cracking of Crude Biodiesel

Before the catalytic cracking was conducted, the crude biodiesel was analyzed by using GCMS. The chromatogram of the crude biodiesel component can be observed in Fig. 3. Methyl linoleate and methyl oleate were found to be the major components in crude biodiesel with the amount of 37.55% and 27.51%, respectively. Aziz et al., [1] also obtained methyl linoleate as the major component of the crude biodiesel with an amount of 39.05%.



Fiure 3. GCMS chromatogram of crude biodiesel

Chromatogram of the catalytic cracking product from crude biodiesel using H-Zeolite and NiO/Zeolite as the catalyst can be seen in Fig. 4, 5, 6, and 7. Biohydrocarbon generated were classified based on the length of the carbon ranging from C_5–C_{11} (biogasoline), C_{12}–C_{15} (biokerosene) and C_{16}–C_{20} (green diesel). There was still an excess of methyl ester which not converted and fatty acid remained. Based on the product constituent obtained from the GCMS, the conversion and the selectivity of the reaction can be determined as seen in Table 2.

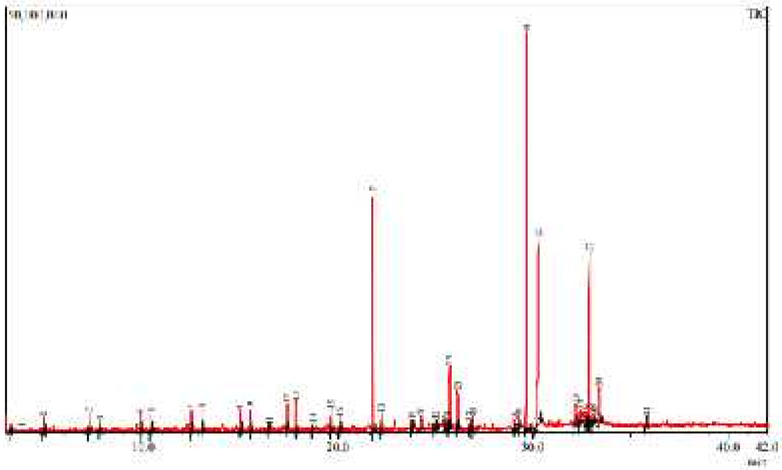


Figure 4. Chromatogram of the product of catalytic cracking using H-Zeolite

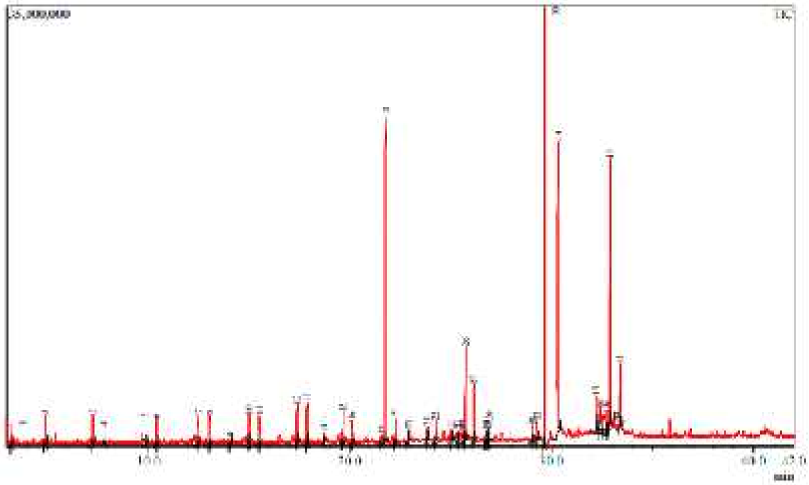


Figure 5. Chromatogram of the product of catalytic cracking using NiO/Zeolite1%

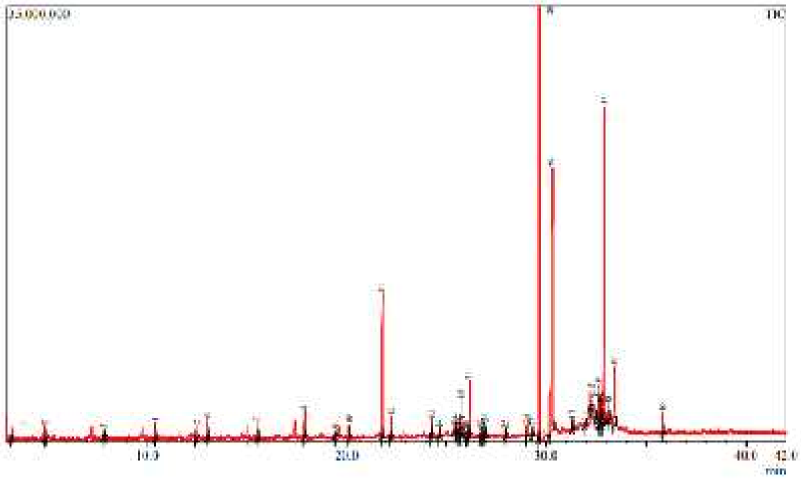


Figure 6. Chromatogram of the product of catalytic cracking using NiO/Zeolite 3%

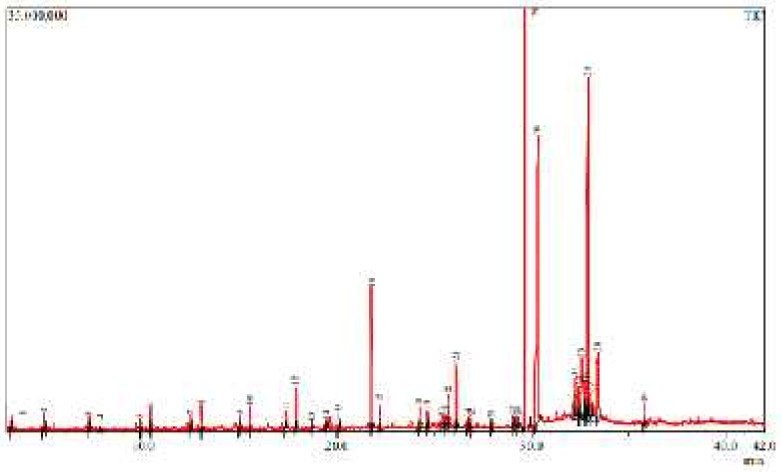


Figure 7. Chromatogram of the product of catalytic cracking using NiO/Zeolite 5%

Table 2. Conversion and selectivity catalytic cracking of crude biodiesel

Catalyst	Conversion (%)	Selectivity of biohydrocarbon (%)		
		Biogasoline	Biokerosine	Green diesel
H-Zeolite	62.76	6.1	14.81	4.27
NiO/Zeolite 1%	60.79	9.73	29.64	9.18
NiO/Zeolite 3%	46.19	5.19	15.55	2.70
NiO/Zeolite 5%	51.74	6.18	13.5	7.16

The highest conversion was obtained by using H-Zeolite with 62.76% conversion. High surface area from the H-Zeolite led to higher conversion. Besides that, H-Zeolite provided Lewis acid sites needed for the cracking catalysis where the other catalyst did not provide these catalytic sites. The catalytic sites accelerated the chain cracking of the crude biodiesel which transformed into biohydrocarbon. Although the conversion achieved by H-Zeolite was higher, the biohydrocarbon selectivity generated from the H-Zeolite was small. The biohydrocarbon total selectivity obtained was 26.99% which consisted of 6.10%, 14.81%, and 4.27% of biogasoline, biokerosene, and green diesel, respectively. Other than biohydrocarbon, H-Zeolite generated higher fatty acids.

The usage of NiO as the active component increased the catalytic activity, as shown in NiO/Zeolite 1%. Ni metal enhanced the catalytic sites hence increased the acidity which acted in the carbon chain cracking [11]. Also, Ni distributed at supporting pores and form the external pores which gave acid sites for the surface of the catalyst [22]. NiO/Zeolite 1% generated the highest biohydrocarbon total selectivity amongst all the catalysts albeit the conversion was smaller than the H-Zeolite. The biohydrocarbon total selectivity of 48.50% was obtained through the NiO/Zeolite 1% which consisted of 9.73%, 29.64, and 9.18% of biogasoline, biokerosene, and green diesel, respectively. The selectivity occurred due to the high surface area exhibited from the catalyst thus maximum selectivity was obtained. Nickel oxide at the zeolite's surface was not distributed well and did not fill the pores of the catalyst. Moreover, the NiO/Zeolite 1% exhibited a higher surface area than the support (H-Zeolite). The lower concentration of NiO (<1%) also did not exhibit the agglomeration or accumulation at the surface of the support, therefore the pores of the catalyst remained intact.

Other than the highest biohydrocarbon total selectivity, the NiO/Zeolite 1% also generated the highest selectivity of biogasoline, biokerosene, and green diesel. This showed that the catalyst was able to break down the crude biodiesel into lighter fractions. The NiO/Zeolite with 3% and 5% composition generated lower biofuel conversion and selectivity than the H-Zeolite. This caused by the lower surface area hence the contact between the reactant and the catalyst was not maximum. Kadarwati et al., [23] obtained a 2% concentration of the Ni/Zeolite catalyst which was the best for the palm oil cracking into biogasoline.

4. Conclusion

Natural zeolite had a similar type of crystallinity to clinoptilolite. Nickel oxide impregnation was not affecting the diffraction pattern of natural zeolite and a few transformationsat the absorption band. NiO/zeolite 1% showed good catalytic activity with the highest conversion of 60.79% and selectivity of gasoline 9,73%; kerosene 29,64% and green diesel 9,18%.

Acknowledgement

The authors thank the Publication and Research Center (Puslitpen), LP2M UIN Syarif Hidayatullah Jakarta which supported the research funding through Applied Research Cluster and Higher Institution Development (Un.01/KPA/233/2018).

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