AJChE 2020, Vol. 20, No. 1, 67 – 76

Solketal Production by Glycerol Acetalization Using Amberlyst-15 Catalyst

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Glycerol, as a by-product of biodiesel production, has recently increased due to the rapid growth of the biodiesel industry. Glycerol utilization is needed to increase the added value of glycerol. Glycerol can be converted to solketal, which can be used as a green fuel additive to enhance an octane or cetane number. Conversion of glycerol to solketal was conducted via acetalization reaction with acetone using amberlyst-15 as the catalyst. The objective of present study was to investigate the effect of some operation conditions on glycerol conversion. Furthermore, it also aimed to develop a kinetic model of solketal synthesis with amberlyst-15 resins. The experiment was conducted in a batch reactor, equipped with cooling water, thermometer, stirrer, and a water bath. The variables that have been investigated in the present work were reaction temperature, reactants molar ratio, catalyst loading, and stirrer speed for 3 hours of reaction time. Temperatures, reactants molar ratio, and stirrer speed appeared to have a significant impact on glycerol conversion, where the higher values led to higher conversion. On the other hand, in the presence of catalyst, the increase of catalyst loading has a less significant impact on glycerol conversion. The results showed that the highest glycerol conversion was 68.75%, which was obtained at 333 K, the reactant's molar ratio was 4, the amount of catalyst was 1 wt%, and stirrer speed of 500 rpm. Based on the pseudo-homogeneous kinetic model, the resulting kinetic model suitable for this glycerol acetalization.

$$\frac{dX}{dt} = k \cdot \exp(\frac{-Ea}{R \cdot T}) \cdot (1-X)^3$$

The value of parameters k and Ea were 1.6135 10^8 min^{-1} and 62.226 kJ mol^{-1}, respectively. The simulation model generally fits the experimental data reasonably well in the temperature range of 313-333 K.

Keywords: Acetone, Amberlyst-15, Fuel additive, Glycerol, Pseudo-homogenous model, Solketal

INTRODUCTION

There has been renewed interest to increase biodiesel production in Indonesia following the plan to introduce B30 as a transportation fuel. As a by-product of biodiesel production, glycerol production will also increase (Qadariyah et al. 2018, Sulistyo et al. 2020). Without proper

DOI: 10.22146/ajche.52455

treatment, glycerol may possess environmental and economic burdens for the industry. Therefore, it is necessary to valorize glycerol with sound production costs.

Solketal is a fuel additive that can be synthesized from glycerol and acetone using the catalyst. For solketal production, a solid catalyst was selected because it is easy to separate and can be used several times. There are numerous works in literature mentioning the role of solid catalyst in solketal production. According to da Silva et al. (2017), SnF_2 appears as a promising solid catalyst for glycerol ketalization. The conversion rate was increased with increasing catalyst loading. Moreover, Barbosa et al. (2019) proposed the use of SiO_2-SO_3H as a catalyst for direct solketal formation by glycerol acetalization with acetone. Furthermore, to improve the catalyst activity, the addition of quaternary ammonium agents could catalyze the di-solketal ether formation. The ketalization of waste glycerol as a side product of biodiesel production can also be conducted with acetone using an amphiphilic catalyst. The conversion of glycerol attained was 73%, with solketal selectivity of 95% (Souza et al. 2015).

Vicente et al. (2010) used acid functionalized SBA-15 as a catalyst for acetalization of crude glycerol. The optimum reaction condition was 343 K and 5% loading of the Ar-SBA-15 catalyst to obtain 90% solketal yields. Unfortunately, the presence of sodium ion content in crude glycerol promoted the deactivation of the sulfonic acid due to reaction between sodium ion and hydrogen ion. Solventless acetalization using mesoporous 5% Nickel-1% Zirconium/Activated Carbon catalyst showed that glycerol conversion increased as the catalyst loading increased (Khayoon and Hameed 2013). By using ethanol as a solvent and amberlyst-35 as the catalyst, Nanda et al. (2014) reported a 75% solketal yield.

Aghbashlo et al. (2019) reported the optimum ketalization condition for solketal synthesis, which corresponds to 308 K by using highly active ZrP-200 solid as the catalyst. The highly active ZrP-200 showed a promising performance with 85.7% glycerol conversion and 98.6% selectivity of solketal at 323 K. It was found that the ZrP-200 showed excellent stability even under mild condition (Li et al. 2019).

Glycerol ketalization with acetone using mordenite solid acid could be promoted by metal ion as a catalyst. Among the metal promoter, Cu-Mo showed better performance than others. It was caused by large acid sites and the insertion effect of the metal particle in the mordenite surface. The glycerol conversion attained was 95% with solketal selectivity of 98% for 15 min reaction time and reactant molar ratio of 3 (Priya et al. 2017).

Manjunathan et al. (2015) investigated an acetalization of glycerol at ambient temperature by using a modified beta zeolite catalyst of 7.5 wt %. It attained 87.1% of the glycerol conversion. They also reported kinetics of solketal synthesis using a pseudo homogeneous model over the zeolite H-BEA catalyst. They assumed the reversible reaction has occurred.

Aghbashlo et al. (2018) carried out an optimization study of a continuous process in solketal production from glycerol and subcritical acetone using Purolite PD 2006 catalyst. The optimal condition was attained at a temperature of 313 K, a reactant ratio of 4.97 with 0.49 mL min^{-1} of fresh feed flow rate. Based on this result, Aghbashlo et al. (2018) proposed the condition for the conversion glycerol for the industrial-scale reactor.

The kinetic for heterogeneous fluid-solid catalytic reaction has been described by several models in the literature, such as Pseudo-Homogeneous (PH), Eley Rideal (ER), Langmuir Hinshelwood Hougen Watson (LHHW) models**.** The simplest model is the Pseudo-Homogeneous model. Nanda et al. (2014) investigated the LHHW model for ketalization glycerol with acetone using the Amberlyst-35 catalyst Meanwhile, Sulistyo et al. (2020) investigated the ER model for ketalization glycerol with acetone using the Indion 225Na catalyst.

The present investigation aims to observe glycerol utilization in solketal production over Amberlyst-15 as a catalyst. The data of glycerol conversion were collected for several parameters. These are reaction temperature, catalyst concentration, reactant molar ratio and mixing speed (Huda 2019, Utami 2019). We also proposed a kinetic model based on a PH model to describe the reaction over a specific temperature range.

EXPERIMENTAL AND MODELING METHODS

Material

Technical glycerol (99.5%) as raw material was purchased from e-Merck. Amberlyst-15 with cation exchange capacity of 5.0 meq/ml, the particle diameter of 0.5mm, the surface area of 53 m^2/g, the pore volume of 0.4 cm^3/g, the average pore diameter of 300 Å. Amberlyst-15 was purchased from Sigma Aldrich. Acetone commercial-grade (99.5%) was used as reactant and purchased from e-Merck.

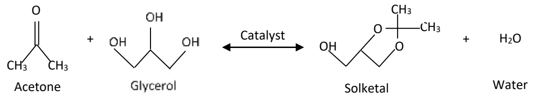
Experimental methods

The experimental setup that has been used in the present investigation is generally similar to Sulistyo et al. (2020). Briefly explained here, the studies were undertaken in a batch reactor equipped with a stirrer and water cooling system. Glycerol was fed into the reactor, then stirrer and heat source was turned on to achieve a targeted temperature. Next, acetone and Amberlyst-15 were fed to the reactor. The investigations were carried out at the temperature range of 313 to 333 K, reactants molar ratio from 3 to 7, catalyst loading from 0 to 7 wt% of glycerol, stirrer speed of 400-700 rpm, and reaction time of 3h.

Every 30 minutes, the sample was taken from the reactor. The liquid and solid catalysts were separated by filtration. The samples were analyzed by AOCS official method Ca 14 – 56 to evaluate the glycerol conversion (Sulistyo et al. 2020)

Kinetics modeling method

The reaction between glycerol and acetone to form solketal can be expressed in Eq. (1) as follows (Nanda et al., 2014):



$$A + G \rightarrow S + W \qquad (1)$$

A glycerol and acetone as reactant were mixed with amberlyst-15 as catalyst has been studied as a catalytic heterogeneous reaction. For kinetics approach, it was proposed a pseudo-homogeneous batch reactor model for heterogeneous catalytic reaction.

$$C_{G0}\frac{dX}{dt} = (-r_G) \tag{2}$$

$$(-r_G) = k_1 {C_A}^m {C_G}^n \tag{3}$$

From the stoichiometry, can be expressed:

$$C_G = C_{G0}(1-X) \tag{4a}$$

$$C_A = C_{A0} - C_{G0}X \tag{4b}$$

$$C_S = C_{G0}X \quad C_{S0} = 0 \tag{4c}$$

$$C_W = C_{G0}X \quad C_{W0} = 0 \tag{4d}$$

Acetone is in excess, then

$$C_{A0} = 4C_{G0} \rightarrow C_{A0} \gg C_{G0} \tag{5a}$$

$$C_A = C_{A0} - C_{G0}X \tag{5b}$$

$$C_A \approx C_{A0} \tag{5c}$$

Eq. (3) can be expressed

$$(-r_G) = k_1 {C_{A0}}^m {C_{G0}}^n\,(1-X)^n \tag{6}$$

Eq (2) can be written in the following equation.

$$C_{G0}\frac{dX}{dt} = k_1 {C_{A0}}^m {C_{G0}}^n\,(1-X)^n \tag{7a}$$

$$\frac{dX}{dt} = k_1 {C_{A0}}^m {C_{G0}}^{n-1}\,(1-X)^n \tag{7b}$$

Arrhenius equation

$$k_1 = A_r \exp(-\frac{E_a}{RT}) \tag{8a}$$

$$k = A_r\, {C_{A0}}^m {C_{G0}}^{n-1} \tag{8b}$$

Finally,

$$\frac{dX}{dt} = k\exp(-\frac{E_a}{RT})\ (1-X)^n \tag{9}$$

In the present study, the value of n has been determined as 3. The objective of parameter estimation was to evaluate the value of k and E_a by minimizing the sum of square error (SSE) of glycerol conversion from the calculation and experimental data (X calculation - X data). Parameter estimation was conducted using lsqnonlin solver in Matlab combined with an ODE solver.

RESULTS AND DISCUSSION

The effect of reaction temperature on glycerol conversion

The impact of the reaction temperature on glycerol acetalization was investigated between 313 to 333 K, as shown in Figure 1. The catalyst loading of 1 wt%, stirrer speed of 500 rpm, and reactant molar of 4 were used, and those parameters were maintained. As presented in Figure 1, the glycerol conversion increased steadily by increasing temperature to attain the highest conversion of 68.75 % at 333 K.

Khayoon and Hameed (2013) synthesized a solketal and found that 45°C or 318 K was the optimal temperature to obtain glycerol conversion close to complete conversion. It can be explained that the transition metal pasted in mordenite and promoted the acetalization of glycerol. It was undertaken at 313 K the glycerol conversion was found to be 81% with solketal selectivity of 88% (Priya et al. 2017). Also, da Silva et al. (2017) presented glycerol ketalization with glycerol conversion close to 90% after 8h reaction at 343 K. Similar result was found when glycerol acetalization with pentanal using HPMo2@Y zeolite catalyst. After 5h, the solketal selectivity was 83% at 303K, 81%

at 323 K, and 80% at 343K (Castanhero et al. 2020).

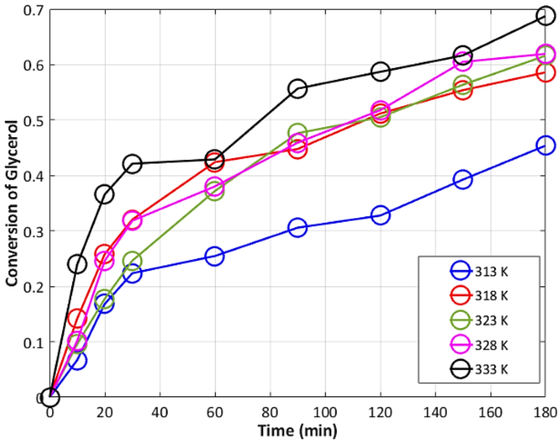


Fig. 1: The effect of reaction temperatures to the glycerol conversion

Although higher temperatures gave higher conversion, it should be noted that higher temperatures may also lower conversion, typically for the exothermic reaction as in agreement to Nanda et al. (2014). Aghbashlo et al. (2019) mentioned that improving reaction temperature may reduce the formation of solketal due to lower acetone concentration as a reactant in the liquid phase. The boiling temperature of acetone was of 333K.

The effect of acetone to glycerol ratio

The impact of the reactants molar ratio on the glycerol conversion was shown in Figure 2. For this section, the catalyst loading of 3 wt%, the temperature of 333 K, and the stirrer speed of 500 rpm were kept constant. The increase of reactants molar ratio gave an increase of glycerol conversion. The various reactant molar ratio from 3, 4, 5, and 7 gave a glycerol conversion 44.7, 50.1, 58.8, and 71.06 %, respectively. Although acetone to glycerol ratio of 7 gave the highest value, the lower value of acetone to glycerol was favorable.

When using Indion 225Na as catalyst and reactant molar ratio from 3 to 10, Sulistyo et al. (2020) found a small increase of glycerol conversion from 17.07% to 19.42%. In other studies, the use of sulfate zirconia catalyst showed a rise of glycerol conversion from 62% to 98% when the reactants molar ratio was increased from 1 to 6 (Castanheiro et al. 2020). As a result of the excess amount of acetone, it would push the solketal formation and improved the complete conversion of glycerol. However, for acetalization of glycerol without catalyst, varying ketone to glycerol ratio did not affect the glycerol conversion (da Silva 2017). By using reactants molar ratio of 1, 2, and 3, Priya et al. (2017) observed the glycerol conversion attained of 81%, 86%, and 86 % with solketal selectivity 79%, 88%, and 95% respectively.

Gadamseti et al. (2015) expressed the effect of the reactant's molar ratio on the solketal selectivity. The reactant's molar ratio was 1, 2, and 3, the selectivity of solketal were fixed of 98%. It can be concluded that the increase in reactants molar ratio does not affect the solketal selectivity. Manjunathan et al. (2015) also pointed out that the reactant's molar ratio of 2 was observed to be the optimum for the formation of solketal. The glycerol conversion was nearly constant, with the increase reactants molar ratio to 3. The solketal selectivity remained almost constant at 98.5%. Khayoon and Hameed (2013) used the reactant molar ratio to be changed from 4 to 8, and glycerol conversion was observed to enhance from

52% to complete conversion. Furthermore, an excess of acetone can also drive the formation of side reaction, such as a six-membered ring acetal. It may be due to the increase of reaction mixture polarity.

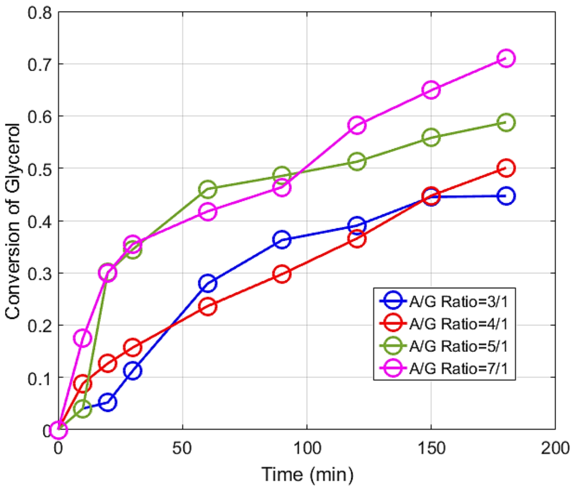


Fig. 2: The effect of acetone to glycerol ratio to the glycerol conversion

The effect of catalyst loading

The effect of catalyst loading experiments was investigated at various concentrations of Amberlyst-15 resin i.e., 1, 3, 5, and 7 wt% of glycerol and also without catalyst. For this variation, the temperature of 333 K, stirrer speed of 500 rpm and reactants molar ratio of 4 were maintained, as shown in Figure 3.

Interestingly, at 180 min (or the end of the experiment), the effect of catalyst loading on glycerol conversion was not significant. For instance, there was a marginal increase in glycerol conversion from 58.44 to 61.28%, with catalyst loading 1 and 3%, respectively. This increase could be associated with the rise in the number of acid sites, which drives glycerol acetalization reaction with acetone to solketal formation. However, at the catalyst loading of 5 and 7%, the glycerol conversion was dropped to 59.02 and 57.46%. It was probably due to precipitation of catalyst in the bottom of the reactor.

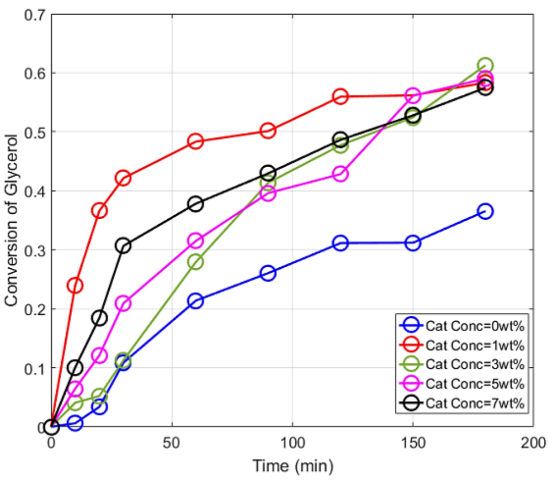


Fig. 3: The effect of catalyst loading to the glycerol conversion

It was also found that the glycerol acetalization reaction without catalyst gave glycerol conversion of 36.56%. Gadamseti et al. (2015) undertaken glycerol acetalization over MoPO/SBA-15 catalyst at ambient temperature. It was observed that 40% MoPO/SBA-15 catalyst gave a high conversion close to complete conversion at low catalyst concentration. The conversion of glycerol was found 87.10% when acetalization by using 7.5 wt% H-Beta-1 catalyst (Manjunathan et al. 2015).

The glycerol acetalization with pentanal using the HPMo2@Y zeolite catalyst was investigated. Castanheiro et al. (2020) found that solketal formation increased with increasing catalyst loading. The solketal selectivity decreased from 84% to 80%, while glycerol conversion increased from 35% to 75%. Reddy et al. (2011) carried out glycerol acetalization by using various catalyst loading to 5 wt%.

They used zirconia and promoted zirconia catalysts. The higher result was observed by using promoted zirconia was 98% of glycerol conversion. As the catalyst loading improved from 3% to 4%, the glycerol conversion was changed from 87% to 100%. Meanwhile, the glycerol conversion was found to be 10% when zirconia catalyst was used.

The effect of mixing speed

The effect of mixing speeds was investigated between 400 to 700 rpm, as presented in Figure 4. The glycerol conversion was found higher as the stirrer speed increased from 400 to 700 rpm. Here, the glycerol conversions were 39.92, 50.08, 55.27, and 61.43%, respectively, at 180 minutes. The increase of stirrer speed from 400 to 700 rpm gave the improvement of glycerol conversion. This result exhibits a different trend compared to our previous study in glycerol acetalization with acetone using the Indion 225Na catalyst (Sulistyo et al. 2020).

In other work, Rosa et al. (2016) carried out the acetalization of glycerol by using the H-BEA catalyst. They mentioned that the impact of external diffusion could be neglected by using higher agitation speed higher than 400 rpm. Under a stirring speed of 750 rpm, there was no effect of mass transfer on the reaction kinetics. Similarly, Khayoon and Hameed (2013) showed that the reaction rate is independent fof the stirring speed above 500 rpm. Therefore, in their experiments, they carried out their experiments at a constant stirring speed of 530 rpm.

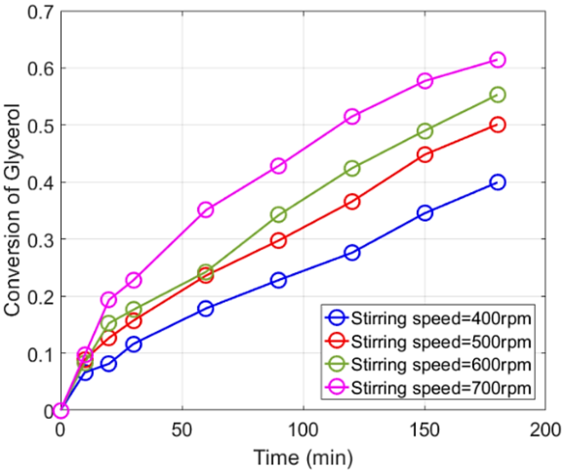


Fig. 4: The effect of mixing speed to the glycerol conversion

The increase of conversion with the increase of stirrer speed, as reported here, might be due to the combined effect of mass transfer and catalytic process that occurs in the reactor. However, no further investigation has been conducted to elaborate on this result.

The kinetics modeling result

The result of kinetic modeling is presented in Figure 5 using a PH model, as in Eq. (9). As shown in Figure 5, it was observed that the model could capture the general trend of glycerol conversion over a temperature range of 313 – 333 K by using catalyst loading of 1 wt.% and stirrer speed of 500 rpm, reactants molar ratio of 4. The model could predict the experimental data relatively well at 313 and 323 K. A larger deviation was observed at 318, 328, and 333 K as the experimental data appeared to be more scattered. The inspection of modeling result from the time horizon shows that the deviation between simulation and experimental data seems to be larger above 60 min.

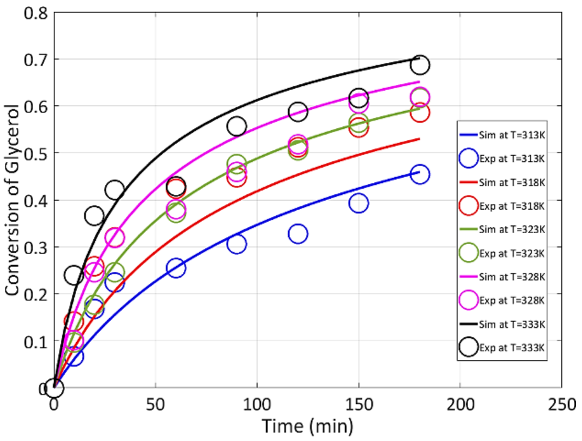


Fig. 5: The result of kinetics modeling as a function of reaction temperature

From parameter estimation using experimental data with temperature variation, the estimated value of k and Ea were 1.6135 10^8 min^{-1} and 62.226 kJ mol^{-1}, respectively. Nanda et al. (2014) reported overall activation energy for glycerol conversion to solketal as high as 55.6 ± 3.1 kJ/mol over Amberlyst 35 catalyst using two parameters of the LHHW model. Hence, the value of Ea reported in the present study shows good agreement with the literature data.

CONCLUSION

The acetalization of glycerol has been carried out using Amberlyst-15 as a catalyst. The influence of temperatures, reactants molar ratio, and stirrer speed appeared to have a significant effect on glycerol conversion. Increasing those factors led to higher glycerol conversion. On the other hand, in the presence of the catalyst, the increase of catalyst loading exhibits no significant impact on glycerol conversion. The observed highest conversion was attained at a temperature of 333 K, reactants molar ratio of 4, catalyst loading of 3 wt% of glycerol and stirrer speed of 500 rpm, which gave 68.75%.

A pseudo-homogeneous kinetic model for describing glycerol acetalization reaction over Amberlyst-15 can be expressed as:

$$\frac{dX}{dt} = k \cdot \exp\left(\frac{-Ea}{R \cdot T}\right) \cdot (1-X)^3$$

The value of parameters k and Ea were 1.6135 10^8 min^{-1} and 62.226 kJ mol^{-1}. The simulation model results gave better accuracy at 313 and 323 K. At other temperatures, the model could still capture the general trend with some deviations.

NOMENCLATURE

A : acetone
A_r : Arrhenius constant [mol^{1-m-n} $L^{m+n-1}$$min^{-1}$]
C_A : acetone concentration [mol L^{-3}]
C_{A_o} : initial acetone concentration [mol L^{-3}]
C_G : glycerol concentration [mol L^{-3}]
C_{G_O} : initial glycerol concentration [mol L^{-3}]
C_S : solketal concentration [mol L^{-3}]
C_{S_O} : initiall solketal concentration [mol L^{-3}]
C_W : water concentration [mol L^{-3}]
C_{W_C} : initial water concentration [mol L^{-3}]
E_a : Activation energy [kJ mol^{-1}]
G : glycerol
k : overall reaction rate constant [min^{-1}]
k_1 : intrinsic reaction rate constant [mol^{1-m-n} $L^{m+n-1}$$min^{-1}$]
m : acetone reaction order
n : glycerol reaction order
R : gas constant [8.314 J mol^{-1} K^{-1}]

r_G : reaction rate of glycerol [mol L^{-3} min^{-1}]
S : solketal
T : temperature [K]
t : time [min]
W : water
X : glycerol conversion

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support by the Ministry of Research, Technology, and Higher Education of Republic of Indonesia under Penelitian Dasar Unggulan Perguruan Tinggi (PDUPT) research grant 2019, under contract number of 124/UN1/DITLIT/DIT-LIT/LT/2019 at Universitas Gadjah Mada.

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