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Utilization of Glycerol by Ketalization Reactions with Acetone to Produce Solketal using Indion 225 Na as Catalyst

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Abstract. The increase of biodiesel production would cause an increase of glycerol as by-products. In the present study, utilization of glycerol by-products to form solketal using Indion 225 Na as a catalyst was investigated. The intrinsic kinetic data were taken in a batch reaction. The results showed that the temperatures and catalyst concentration have a significant influence on the conversion of glycerol. However, varying the acetone to glycerol ratio only had a marginal impact on glycerol conversion. A kinetic model based on Eley Rideal mechanism was developed to describe the reaction mechanism over the catalyst. The simulation results of glycerol conversion were compared to experimental data at temperatures from 308 K to 328 K. From the kinetic model, it was found that the pre-exponential factor of 2.59 min^{-1}, activation energy of 21.16 kJ/mol, acetone adsorption equilibrium of 0.62, and solketal desorption equilibrium of 0.03 were obtained. Comparison between the experimental and calculated glycerol concentrations showed that the model described the data well within the temperature range of 308 K to 328 K.

Keywords: Acetone; Catalyst; Glycerol; Kinetic; Solketal

1. Introduction

There has been growing interest in increasing the use of biodiesel as a renewable transportation fuel in Indonesia. According to the National Energy Plan (2017), Indonesia is expected to increase the portion of renewable energy from 23% of total energy consumption in 2025 to 31.2% in 2050. The increase use of renewable energy is an important step for Indonesia as it strives to decrease its greenhouse gas emissions. The increase of biodiesel production in the country will be accompanied by a corresponding increase of glycerol as a by-product of biodiesel production. Typically, glycerol yields as high as 10 wt% from transesterification reactions are obtained during biodiesel production. Therefore, there is an urgent need to utilize glycerol as a raw material to produce value-added chemicals along with the increase of biodiesel production.

Many studies have reported the conversion of glycerol to produce various chemicals. Tan et al. (2013) and Kong et al. (2016) proposed glycerol conversion to 1,3-propanediol which plays an important role on production of polymers, cosmetic, food, lubricants and medicine. In addition, it can be converted to acrolein as an intermediate of acrylic acid production. Glycerol can also be converted to hydrogen and syngas as a platform for various

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chemicals production. A plasma electrolysis method to produce hydrogen was reported by Saksono et al. (2012). Regarding hydrogen production from glycerol, Slamet et al. (2015) used a TiO2 P25 photocatalyst modified with metals such as Platinum (Pt), Copper (Cu), and non–metal Nitrogen doping.

In another study, Leong et al. (2016) reported the pyrolysis of crude glycerol using a microwave heating technique to produce pyrolyzed liquid, which can be used as fuels in combustion systems. Glycerol could also be converted to glycerol carbonate (Okoye and Hameed, 2016). Glycerol carbonate is known as a green organic solvent, which has a high boiling point. Ketalization of glycerol with acetone to produce an oxygenated compound such as solketal is an interesting question to consider, as solketal is known as a promising fuel additive (Reddy et al., 2011; Nanda et al., 2016).

Solid catalyst is generally preferred for solketal production as it improves the separation of catalyst. Specifically, zirconia and promoted zirconia catalysts have been used for the ketalization of glycerol (Reddy et al., 2011). Reddy et al. (2011) reported the promoted zirconia catalyst exhibited promising catalytic activity with the highest glycerol conversion of 98% using a sulphate zirconia catalyst at room temperature. da Silva et al. (2017) used SnF_2 as catalyst for the ketalization of glycerol with propanone to form solketal to obtain ca. 97% of glycerol conversion at ambient temperature. Nanda et al. (2014) reported on the use of ethanol as a solvent in glycerol acetylation using Amberlyst 35 as a catalyst, which produced a solketal yield as high as 74%. The mesoporous 5% Ni-1%Zr/AC catalyst has also been used for acetalization of glycerol without solvent, which yielded complete glycerol conversion (Khayoon and Hameed, 2013). Some catalysts, such as zeolite Beta, Amberlyst 15, and p-toluene sulfonic acid, have also been used for glycerol acetalization with acetone (da Silva et al., 2009). The results showed that the zeolite Beta with a high ratio of Si to Al attained a glycerol conversion of more than 95%. It was also found that the high ratio of Si to Al is beneficial as it caused the zeolite to block the entry of water into the pores.

Temperatures higher than 313 K are typically needed to obtain sufficient conversion to force water removal and to drive the forward reaction to produce solketal (Esteban et al., 2015). Vicente et al. (2010) investigated acetalization using crude glycerol with an SBA-15 catalyst and found high glycerol conversion. To drive the reaction equilibrium, they proposed a new method for water removal by refluxing the flask followed by water vaporization under vacuum pressure. Manjunathan et al. (2015) also produced solketal by reacting glycerol with acetone at an ambient temperature by using a modified beta catalyst. They obtained a glycerol conversion of 87.1% by using a catalyst loading of 7.5%. The pseudo homogeneous kinetics model for ketalization of glycerol using H-BEA as a catalyst was proposed by Rossa et al. (2017). At a temperature range of 313 K to 353 K, the activation energies for forward and reverse reactions were 44.77 kJ/mol and 41.40 kJ/mol, respectively. Nanda et al. (2014) investigated the kinetics of ketalization of glycerol at 293-323 K with Amberlyst 35 as a catalyst. They proposed a Langmuir-Hinshelwood kinetic model and obtained an activation energy of 55.6 kJ/mol. Overall, these studies show that the temperatures between 300-350 K are needed for glycerol conversion. As a result, kinetics studies with solid catalyst should be investigated within that range of temperatures.

The purpose of the present study was to develop a kinetics model of solketal synthesis from glycerol and acetone over an Indion 225 Na catalyst. Indion 225 Na is known to be an inexpensive ion exchanger compared to Amberlysts, and it is more accessible on the market. To achieve our proposed aim, glycerol conversion data were taken while varying reaction conditions such as temperature, catalyst concentration, stirrer speed, and acetone to glycerol ratios (Priadana, 2017; Fitriandini, 2017).

2. Experimental and Modelling Methods

2.1. Materials

Glycerol technical grade (85.5 wt%) was purchased from CV Brataco Chemical. The glycerol used was further purified by water evaporation to reach 98.6 wt%. The Indion 225 Na resin used for the catalyst was purchased from CV General Labora. Indion 225 Na has a cation exchange capacity of 2.0 meq/ml. Commercial grade (99.5 wt%) acetone (Sigma Aldrich) was obtained from CV Multi Kimia.

2.2 Experimental Procedure

The experiments were performed using a three necks flask equipped with a stirrer and condenser system as a batch reactor. First, glycerol was fed to the flask; then, it was stirred and heated to the attained temperature. Next, acetone and Indion 225 Na resin were added to the flask. Samplings were taken every 0.5 hours. Subsequently, the liquid sample was separated from the solid catalyst prior to analysis of glycerol content. The glycerol content was analysed using the AOCS official method Ca 14-56. The conversion of glycerol was estimated by taking the ratio between the amount of glycerol converted at various time and initial glycerol concentrations.

2.3 Kinetics Modelling

The mechanism of reaction rate for the acetalization reaction was derived by Manjunathan et al. (2015), and from their findings, they proposed the Eley-Rideal mechanism. The reaction steps of this model can be expressed as follows.

1. In the first step, the carbonyl group in acetone was activated by acid sites of the catalyst.

$$\mathrm{Ac} + \mathrm{s} \rightarrow \mathrm{Acs} \tag{1}$$

2. The OH group of glycerol attacks the adsorbed carbonyl to form an intermediate product such as hemiacetal.

$$\mathrm{Acs} + \mathrm{G} \rightarrow \mathrm{Hs} \tag{2}$$

3. The hemiacetal undergoes cyclization to facilitate formation of adsorbed solketal and water.

$$\mathrm{Hs} \rightarrow \mathrm{Ss} + \mathrm{W} \tag{3}$$

4. Adsorbed solketal is desorbed from the surface active of the catalyst.

$$\mathrm{Ss} \rightarrow \mathrm{S} + \mathrm{s} \tag{4}$$

The result of the reaction rate mechanism can be expressed as follows:

$$r_s = \frac{k \cdot \left(C_A \cdot C_G - \dfrac{C_S \cdot C_W}{K_{eq}}\right)}{1 + K_A \cdot C_A + K_S \cdot C_S} \tag{5}$$

$$K_{eq} = \exp\left(3.6154 \cdot 10^3 \cdot \frac{1}{T(K)} - 11.308\right) \tag{6}$$

$$k = A \cdot \exp\left(\frac{-Ea}{R \cdot T(K)}\right) \tag{7}$$

Equation 5 presents the reaction rate for solketal formation from acetone and glycerol. This equation was then incorporated with the batch reactor model. There were four parameters: the pre-exponential factor (A), activation energy (Ea), acetone adsorption constant, K_A, and solketal desorption constant, K_S. In addition, the equilibrium constant is presented as a function of temperature, as shown in Equation 6 (Nanda et al., 2014). Parameters A, Ea, K_A and K_S in Equation 6 were estimated by non-linear regression to minimize the SSE of glycerol conversion based on simulation and experimental data. Parameter fitting and simulation were conducted in MATLAB with gradient search methods (lsqnonlin) and ODE solver. The initial concentrations of acetone and glycerol used for the simulation were 11.25 and 2.25 M, respectively.

3. Results and Discussion

Solketal synthesis was conducted by reacting glycerol with acetone catalysed by Indion 225 Na resin. The reaction was conducted at a temperature of 308 K to 328 K, with a catalyst loading up to 7wt% of glycerol, a stirrer speed between 500 to 800 rpm, a molar ratio of acetone to glycerol from 3 to 10, and a reaction time of 3 h.

3.1. The Influence of Reaction Temperature

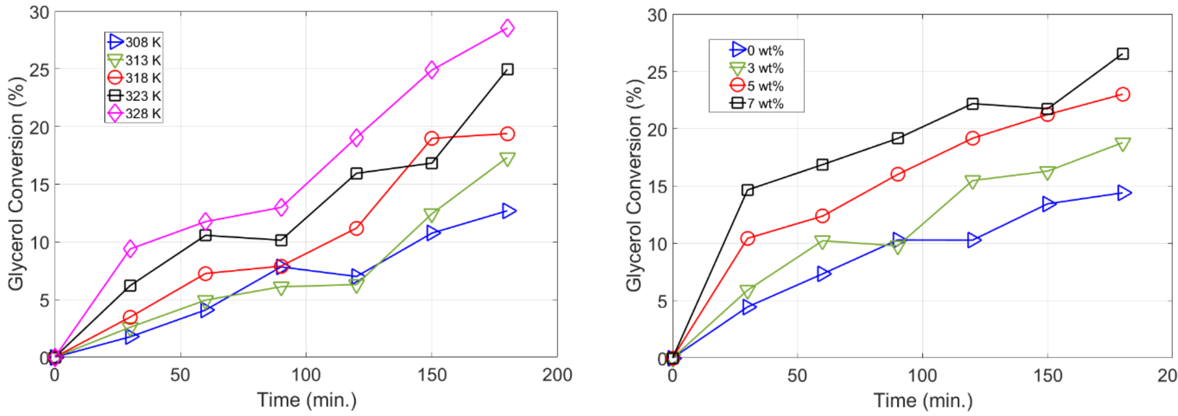
Temperature parameters affect the reaction rate and the equilibrium of chemical reactions. The effect of the reaction temperature on glycerol ketalization with acetone was investigated between 308 K and 328 K, with a 5 K interval, as presented in Fig 1a. Here, the catalyst loading of 5 wt%, stirrer speed of 500 RPM, and molar ratio of acetone to glycerol of five were used, and those parameters were kept constant. Fig. 1a shows that the glycerol conversion increased steadily as temperature increased to reach the maximum conversion of 28.50% at 328 K.

From the literature, it is evident that the synthesis of solketal using a Ni-Zr/AC catalyst was most effective at a temperature of 318 K to give the highest glycerol conversion (100%) with selectivity of 74% for six acetal products (Khayoon and Hameed, 2013). In addition, da Silva et al. (2017) presented glycerol ketalization using solid acid catalyst with glycerol conversion up to 90% after 8 h reaction at 343 K. In sum, for ketalization of glycerol, the increase of temperature is favourable as it gives higher glycerol conversion along with higher selectivity in the formation of 5 numbered cyclic acetal (Trifoi et al., 2016). Yet, Esteban et al. (2015) pointed out that temperatures higher than 313 K were always required to facilitate solketal formation. Shirani et al. (2014) and Nanda et al. (2014) mentioned that the temperature increase could also be disadvantageous, as it may lower the solketal yield. This occurs at certain temperatures when acetone started to vaporize, leaving the glycerol in the reaction system, which ultimately results in less contact between the gaseous acetone molecules and the liquid glycerol molecules on the catalyst surface. As a result, this condition leads to a reduction of solketal formation, which is indicated by lower yield as well as lower conversion.

3.2. The Influence of Catalyst Concentration

The influence of catalyst concentrations was measured by varying the loading of Indion 225 Na resin from 0 wt% to 7 wt% according to glycerol weight. For this variation, the stirrer speed of 600 RPM, molar ratio of acetone to glycerol of five, and temperature of 328 K were maintained. Figure 1b shows the glycerol conversion by varying catalyst concentration. As shown in Fig 1b, the glycerol conversion was significantly increased from 18.74% to 26.55% with the increase in catalyst loading from 1 to 7 wt%. The increase in conversion might be due to the increase of accessible active sites that facilitate glycerol conversion to solketal. It was also found that reaction without a catalyst gave glycerol conversion of 14.41%.

Manjunathan et al. (2015) conducted glycerolysis with acetone by using H-Beta-1 as a catalyst, and they attained a glycerol conversion of 87.10% with a catalyst concentration of 7.5 wt%. Meanwhile, Vicente et al. (2010) undertook the acetalization of high-grade glycerol with acetone using Ar-SBA-15 as a catalyst. This chemical was found to deliver excellent catalytic behaviour (Vicente et al., 2010). The experiment was done by using reflux with a reaction temperature of 343 K and a catalyst weight of 5 wt% based on glycerol; under these conditions, the glycerol conversion reached 80% after only 15–30 minutes. Reddy et al. (2011) undertook an acetalisation of glycerol with zirconia and promoted a zirconia catalyst. The promoted zirconia catalyst amount increased up to 5 wt%, and a glycerol conversion of 100% was attained. Higher catalyst loading resulted in a faster initial reaction rate, and a higher amount of active sites facilitated activation of carbonyl group of ketones.



(a) (b)

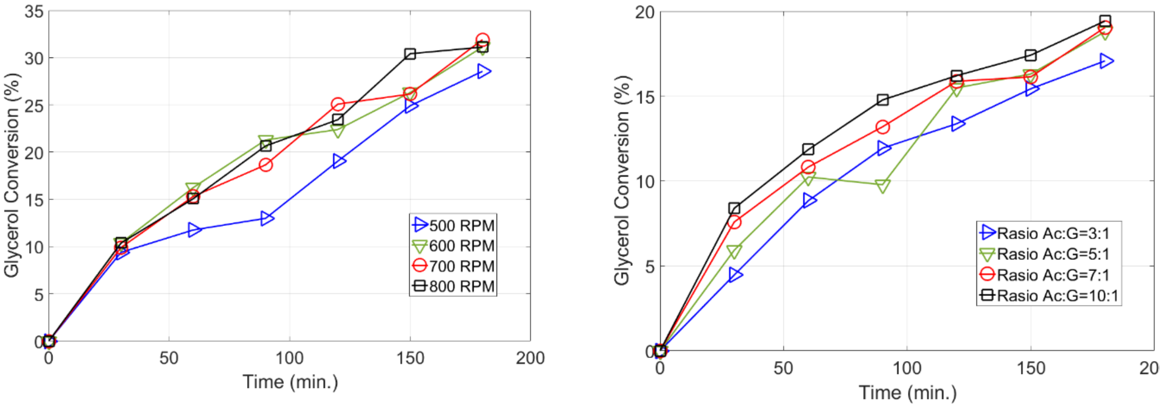
Figure 1 The influence of reaction temperatures (a) and catalyst concentration (b) on glycerol conversion

3.3. The Influence of Stirrer Speed

The influence of stirrer speeds was investigated from 500 to 800 rpm. For this variation, the catalyst loading of 5 wt%, molar ratio of acetone to glycerol of five, and temperature of 328 K were kept constant. The glycerol conversion is shown in Figure 2a. As the stirrer speed increased from 500 to 800 rpm, the glycerol conversions were 28.55 (500 rpm), 31.12 (600 rpm), 31.90 (700 rpm), and 31.11% (800 rpm). At a stirrer speed between 600 and 800 rpm, there were no appreciable changes in glycerol conversion. Agirre et al. (2013) conducted experiments using a stirring speed of 750 rpm and 1250 rpm for reacting glycerol with acetaldehyde. They reported that there was no influence of stirring rate on the reaction kinetics. These results were supported by Nanda et al. (2014), who investigated ketalization of glycerol with stirring speeds of 400 rpm and 1100 rpm. They found that with consistent conditions (i.e., a temperature of 323 K, a molar ratio of acetone to glycerol of two, and catalyst concentration of 1 wt% of glycerol), stirring speeds of 400 rpm and 1100 rpm resulted in the same equilibrium yield of solketal of 60%. In addition, they have also found that both stirrer speed of 400 rpm and 1100 rpm gave similar initial formation rate of solketal which was evident from the slope of solketal yield and time (Nanda, et al. 2014). Similarly, Hong et al. (2013) showed that reaction rate is not influenced by the agitation speed above 500 rpm. At the agitation speed of 500 rpm, the conversion is almost 50% lower than the conversion at the stirring speed of 800 rpm. The effect of external mass transfer on glycerol ketalization when using a solid catalyst such as sulphonic ion exchange resin can be overcome by using stirring speeds above 700 rpm (Esteban et al. 2015). Hence, it may be concluded that at high stirring rate, the mass transfer resistance can be neglected and the chemical reaction step can be inferred as the rate controlling step or in other words it is under the kinetic regime. Trifoi et al. (2016) highlighted that the mixing operation is affected by various parameters: the reactant's properties, the product's properties, the molar ratio between reactants, and the parameters related to the reactor operation, such as power of agitation, batch or continuous mode, and the equipment used. In addition, the stirring speed has no effect on the reaction kinetics if the reactants are in high excess.

3.4 The Influence of Molar Ratio of Acetone to Glycerol

The influence of the molar ratio of acetone to glycerol on glycerol conversion over Indion 225 Na resins as a catalyst is presented in Figure 2b. For this variation, the catalyst concentration of 3 wt%, temperature of 323 K, and stirrer speed of 600 rpm were kept constant. It was observed that an increase in the molar ratio of acetone to glycerol would drive the solketal formation. Increasing the molar ratio of acetone to glycerol from 3 to 10 led to a small increase of glycerol conversion from 17.07% to 19.42%. Esteban et al. (2015) reported that increasing the molar ratio of acetone to glycerol from 3 to 12 enhanced the glycerol conversion from 34% to approximately 96%. Additionally, Reddy et al. (2011) showed that glycerol acetalisation using a sulphate zirconia catalyst obtained a glycerol conversion of 62% and 98% at molar ratios of 1:1 and 6:1, respectively. da Silva et al. (2009) proposed a reversible reaction on ketalization of glycerol. They found that an excess of acetone would lead to increased solketal formation and complete conversion of glycerol. However, in the absence of a catalyst, the varying ketone to glycerol molar ratio did not affect significant change in glycerol conversion (da Silva et al., 2017). The equilibrium conversion of the formaldehyde increased with increasing glycerol to formaldehyde molar ratio. Agirre et al. (2013) investigated ketalization of glycerol with formaldehyde in excess glycerol. This led to 100% conversion of formaldehyde. However, changes in the molar ratio of acetone to glycerol did not prove to affect the selectivity of 5 cyclic of acetal. Manjunathan et al. (2015) also obtained a similar glycerol conversion for a 2:3 molar ratio of acetone to glycerol. Moreover, they mentioned that a molar ratio of acetone to glycerol of two was the optimum condition for the catalytic reaction of solketal production. The solketal selectivity also remained constant at 98.5%. Similarly, with the use of SnF_2 catalyst, the glycerol conversion increased up to 97% when the molar ratio of ketone to glycerol was eight or higher at ambient temperature. In this case, the solketal selectivity was higher than 90% (da Silva et al. 2017). Khayoon and Hameed (2013) reported that as the molar ratio of acetone to glycerol was raised from four to eight, glycerol conversion increased from 52% to 100%. However, the selectivity to five solketal was decreased. Furthermore, an excess of acetone drove 6 cyclic acetal formation.



(a) (b)

Figure 2 The effect of stirrer speed (a) and acetone to glycerol ratio (b) on glycerol conversion rates

3.5 *Kinetic Modelling Result*

In the present study, the Eley-Rideal mechanism was proposed for kinetics modelling. The surface reaction as the rate-limiting step has been proposed as in Equation 5. Figure 3 presents the simulation results and the experimental data. For non-linear regression with lsqnonlin solver in MATLAB, we have used initial guess of 1, 20, 1 and 1 for A, Ea, K_A and K_S, respectively.

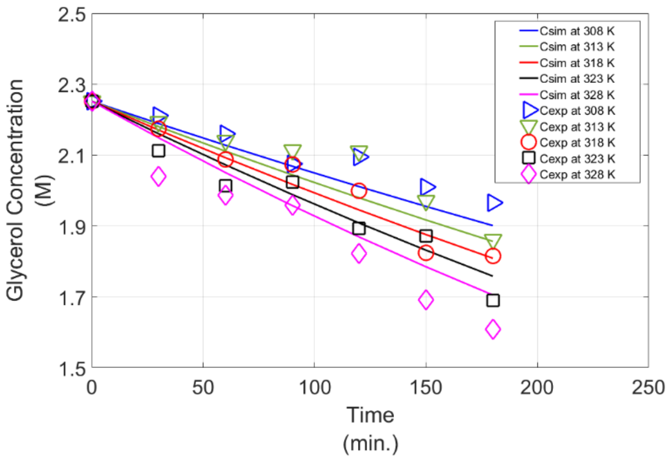


Figure 3 Glycerol concentration versus time for simulation result and experimental data at 308–328 K

As seen in Figure 3, in general, the model captured the decrease in glycerol concentrations as a function of reaction time at various temperatures. At 308 K, the model underestimated the glycerol concentrations. It could predict the glycerol concentration better at the reaction temperature of 313 K to 323 K. In contrast, at 328 K, the model overestimated the glycerol concentrations. Overall, it is evident that the model could be used as a tool to predict glycerol concentration within the temperature range used in the present study.

The modelling work also allowed us to estimate kinetics parameters. Parameters A, Ea, K_A, and K_S were calculated at temperatures ranging from 308 K to 328 K. From parameter calculations, a pre-exponential factor of 2.59 min^{-1}, activation energy of 21.16 kJ/mol, acetone adsorption equilibrium of 0.62, and solketal desorption equilibrium of 0.03 were obtained. The activation energy for solketal production calculated in this investigation is lower than that found by Nanda et al. (2014), who reported an activation energy of 55.60 kJ/mol when using Amberlyst 35 as a catalyst. It was also lower than that found by Rossa et al. (2017), which showed a required forward reaction energy activity of 44.77 kJ/mol. In general, lower activation energy means that less energy is required for the reaction to occur. However, the requirements to achieve high conversion depend not only on the activation energy. Other factors such as catalyst activity (active sites), collision factor, reactant concentrations, and temperatures also play a role in achieving high conversion of glycerol.

4. Conclusions

The acetalization of glycerol has been investigated in the present study by using the ion exchange resin Indion 225 Na. Temperature and catalyst loading significantly influenced the glycerol conversion rate. However, the molar ratio of acetone to glycerol had negligible effects on the solketal formation. The influence of stirrer speed was also negligible. As a result, it confirmed the absence of mass transfer resistance under high stirring rate. Thus, the reaction rate can be assumed to be measured under kinetic regime. A kinetic model based on the Eley-Rideal mechanism was developed to describe the reaction mechanism over the catalyst. The simulation results were compared to glycerol experimental data at temperatures ranging from 308 K to 328 K. From parameter calculations, we found a pre-exponential factor of 2.59 min^{-1}, an activation energy of 21.16 kJ/mol, an acetone adsorption equilibrium of 0.62, and solketal desorption equilibrium of 0.03. Comparison of glycerol concentrations between the simulated and experimental data showed that the model could describe the data well within the temperature range of 308-328 K.

Notations

A : pre-exponential factor
Ac : acetone
Acs : acetone adsorbed on the surface active
C_A : concentration of acetone in bulk liquid, mol L^{-1}
C_G : concentration of glycerol in bulk liquid, mol L^{-1}
C_H : concentration of hemiacetal in the catalyst, mol L^{-1}
C_S : concentration of solketal in bulk liquid, mol L^{-1}
Ea : activation energy, J mol^{-1}
G : glycerol
Hs : hemi acetal adsorbed on the surface active
k : reaction rate constant, min^{-1}
K_{eq} : ketalization equilibrium constant
K_A : acetone adsorption equilibrium constant
K_S : solketal desorption equilibrium constant
R : gas constant, 8.14 Jmol^{-1}K^{-1}
r_s : surface reaction rate
S : solketal
Ss : solketal adsorbed on the surface active
s : catalyst surface active site
T : temperature, K
W : water

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References

Agirre, I., Güemez, M.B., Ugarte, A., Requies, J., Barrio, V.L., Cambra, J.F., Arias, P.L., 2013. Glycerol Acetals as Diesel Additives: Kinetic Study of the Reaction between Glycerol and Acetaldehyde. *Fuel Processing Technology*, Volume 116, pp. 182–188

da Silva, C.X.A., Goncalves, V.L.C., Mota, C.J.A., 2009. Water Tolerant Zeolite Catalyst for the Acetalization of Glycerol. *Green Chemistry,* Volume 11(1), pp. 38–41

da Silva, M.J., Rodrigues, F.A., Julio, A.A., 2017. SnF_2-Catalyzed Glycerol Ketalization: A Friendly Environmentally Process to Synthesize Solketal at Room Temperature Over on Solid and Reusable Lewis Acid. *Chemical Engineering Journal*, Volume 307, pp. 828–835

Esteban, J., Ladero, M., Garcia-Ochoa, F., 2015. Kinetic Modelling of the Solventless Synthesis of Solketal with a Sulphonic Ion Exchange Resin*.* *Chemical Engineering Journal,* Volume 269, pp. 194–202

Fitriandini, Y.W., 2017. *Solketal Synthesis from Glycerol and Acetone using Indion 225 Na as Catalyst (the Effect of Temperature and Stirring Speed).* Research Report of Chemical Reaction Engineering and Catalysis Lab., Department of Chemical Engineering, Universitas Gadjah Mada, Yogyakarta, Indonesia

Hong, X., Mc Giveron, O., Kolah, A.K, Orjuela, A., Peereboom, L., Lira, C.T., Miller, D.J., 2013. Reaction Kinetics of Glycerol Acetal Formation via Transacetalization with 1,1-diethoxyethane. *Chemical Engineering Journal*, Volume 222, pp. 374–381

Khayoon, M.S., Hameed, B.H., 2013. Solventless Acetalization of Glycerol with Acetone to Fuel Oxygenates over Ni-Zr Supported on Mesoporous Activated Carbon Catalyst. *Applied Catalysis A: General*, Volume 464-465, pp. 191–199

Kong, P.S., Aroua, M.K., Wan Dawud, W.M.A., 2016. Conversion of Crude Glycerol and Pure Glycerol into Derivatives: A Feasibility Evaluation. *Renewable and Sustainable Energy Reviews,* Volume 63, pp. 533–555

Leong, S.K., Lam, S.L., Ani, F.N., Ng, J., Chong, C.T., 2016. Production of Pirolyzed Oil from Crude Glycerol using a Microwave Heating Technique. *International Journal of Technology,* Volume 7(2), pp. 323–331

Manjunathan, P., Maradur, S.P., Halger, A.B., Shanbhag, G.V., 2015. Room Temperature Synthesis of Solketal from Acetalization of Glycerol with Aceton: Effect of Crystallite Size and the Role of Acidity of Beta Zeolite. *Journal of Molecular Catalysis A: Chemical,* Volume 396, pp. 47–54

Nanda, M.R., Yuan, Z., Qin, W., Ghaziaskar, H.S., Poirier, M.A., Xu, C., 2014. Thermodynamic and Kinetic Studies of a Catalytic Process to Convert Glycerol into Solketal as an Oxygenated Fuel Additive. *Fuel,* Volume 117 Part A, pp. 470–477

Nanda, M.R., Zhang, Y., Yuan, Z., Qin, W., Ghaziaskar, H.S., Xu, C., 2016. Catalytic Conversion of Glycerol for Sustainable Production of Solketal as a Fuel Additive: A Review. *Renewable and Sustainable Energy Reviews,* Volume 56, pp. 1022–1031

Okoye, P.U., Hameed, B.H., 2016. Review on Recent Progress in Catalytic Carboxylation and Acetylation of Glycerol as a Byproduct of Biodiesel Production. *Renewable and Sustainable Energy Reviews*, Volume 53, pp. 558–574

Priadana, D.P., 2017. *Solketal Synthesis from Glycerol and Acetone using Indion 225 Na as Catalyst (the Effect of Catalyst Concentration and Molar ratio of Acetone to Glycerol). Research Report of Chemical Reaction Engineering and Catalysis Lab.,* Department of Chemical Engineering, Universitas Gadjah Mada, Yogyakarta, Indonesia

Reddy, P.S., Sudarsanam, P., Mallesham, B., Raju, G., Reddy, B.M., 2011. Acetalisation of Glycerol with Acetone over Zirconia and Promoted Zirconia Catalysts under Mild Reaction Conditions. *Journal of Industrial and Engineering Chemistry*, Volume 17(3), pp. 377–381

Rossa, V., Pessanha, Y.S.P., Diaz, G.C., Camara, L.D.T., Pergher, S.B.C., Aranda, D.A.G., 2017. Reaction Kinetic Study of Solketal Production from Glycerol Ketalization with Acetone. *Industrial and Engineering Chemistry Research*, Volume 56(2), pp. 479–488

Saksono, N., Ariawan, B., Bismo, S., 2012. Hydrogen Production System using Non-thermal Plasma Electrolysis in Glycerol-KOH Solution. *International Journal of Technology,* Volume 3(1), pp. 8–15

Shirani, M., Ghaziaskar, H.S., Xu, C., 2014. Optimization of Glycerol Ketalization to Produce Solketal as Biodiesel Additive in Continuous Reactor with Subcritical Acetone using Purolite PD206 as Catalyst. *Fuel Processing Technology*, Volume 124, pp. 206–211

Slamet, S., Kusrini, E., Afrozi, A.S., Ibadurrohman, M., 2015. Photocatalytic Hydrogen Production from Glycerol-water over Metal Loaded and Non-metal Doped Titanium Oxide. *International Journal of Technology,* Volume 6(4), pp. 520–532

Tan, H.W., Abdul Azis, A.R., Aroua, M.K., 2013. Glycerol Production and Its Applications as a Raw Material: A Review. *Renewable and Sustainable Energy Reviews,* Volume 27, pp. 118–127

Trifoi, A.R., Agach, P.S., Pap, T., 2016. Glycerol Acetals and Ketals as Possible Diesel Additives. A Review of Their Synthesis Protocols, *Renewable and Sustainable Energy Reviews*, Volume 62, pp. 804–814

Vicente, G., Melero, J.A., Morales, G., Paniagua, M., Martin, E., 2010. Acetalisation of Bio-Glycerol with Acetone Produce Solketal over Sulfonic Mesostructured Silicas. *Green Chemistry.* Volume 12(5), pp. 899–907