Reaktor

p-ISSN 0852 – 0798
e-ISSN 2407 – 5973

Acredited: SK No.: 60/E/KPT/2016
Website : http://ejournal.undip.ac.id/index.php/reaktor/

Reaktor, Vol. 18 No. 1, March Year 2018, pp. 1-6

The Kinetics of Calcium Oxide Catalyzed Esterification of Glycerol with Free Fatty Acids Using Pseudo-homogeneous Model Approach

Megawati*), Dhoni Hartanto, Catur Rini Widyastuti, Diyah Saras Wati and Eny Nurhayati

Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang
Sekaran, Gunungpati, Semarang 50229, Indonesia
Telp./Fax. (024)8508101/(024)8508009

*)Coresponding author: megawati@mail.unnes.ac.id

(Received: September 04, 2017; Accepted: February 02, 2018)

Abstract

This research aims to study the reaction kinetics of esterification reaction of glycerol with free fatty acid (FFA) using calcium oxide catalyst to produce mono-diacylglycerol (MDAG) using pseudo-homogeneous approach. The effects of time and temperature on the reaction conversion were investigated simultaneously. The FFA used was from the waste of cocoa production process, while the solid catalyst used was calcium oxide from eggshell ash. The results show that the cocoa based FFA was composed of palmitic acid (49.24%), methyl stearate (1.05%), oleic acid (25.39%), and stearic acid (24.32%). The calcium oxide content in the eggshell ash was 60% w/w. At all temperatures studied (60, 70, and 80^{o}C), as the reaction time increased, the conversion increased sharply in the first 5 minute followed by a gradual raise to an almost constant value after 20 minutes (0.844; 0.845; and 0.854, respectively). Pseudo-homogeneous second order model can describe the reaction kinetics satisfactorily. The reaction constants (k) at 60, 70, and 80^{o}C were 0.00384, 0.003401, and 0.003518 (L/mole.minute), respectively. The effects of temperature on reaction rate obey the Arrhenius' equation with collision factor (A) is 0.2659 (L/mole.minute) and activation energy (Ea) is 3544 J/mol.

Keywords: *calcium oxide; free fatty acid; glycerol; pseudo-homogeneous approach*

How to Cite This Article: Megawati, Hartanto, D., Widyastuti, C.R., Wati, D.S., and Nurhayati, E., (2018), The Kinetics of Calcium Oxide Catalyzed Esterification of Glycerol with Free Fatty Acids Using Pseudo-homogeneous Model Approach, Reaktor, 18(1), 1-6, http://dx.doi.org/10.14710/reaktor.18.1.1-6

INTRODUCTION

Cocoa is one of important commodities of Indonesia, which can be processed into various products, such as beverages, cosmetics, pharmacies, and healthy supplements (anti-inflammation, anti-microbes, anti-carcinogenic, and analgesics). One of cocoa processing industry wastes is FFA (free fatty acid) (Lasisi, 2014). The FFA waste can be converted into palm fatty acid distillate (PFDA) which can be used as raw material of cream detergent (Rumondang, 2016). The FFA waste of cocoa contains palmitic, oleic, methyl stearic, and stearic acids (Indarti, 2007). Reaction of FFA with glycerol will produce monodiacylglycerol (MDAG) (Akoh and Min, 2002; Huang *et al.*, 2013; Setyaningsih *et al.*, 2016), which can be utilized as food emulsifier (Hasenhuettl, 2008; Huang *et al.*, 2013; Kurniasih, 2014). The MDAG is the most widely used synthetic emulsifier in food industries, amounting up to 70% (Triana, 2014). The other product, such as the diacylglycerol is a safe and healthy food additive recognized by the US Food and Drug Administration (Wang *et al.*, 2011).

A number of reports have been devoted to research on MDAG synthesis from PFAD and various vegetable oils (soy-oil, corn oil, and palm oil) (Rumondang, 2016; Purba *et al.*, 2014). Rumondang (2016) synthesized MDAG using glycerol and PFAD. Purba *et al.* (2014) studied the effect of eggshell ash amount and glycerolysis reaction time on the conversion of MDAG using tert-butanol as a co-solvent. Generally, MDAG is produced through alkali or enzyme catalyzed esterification and glycerolysis (Huang *et al.*, 2013; Kurniasih, 2014; Watanabe *et al.*, 2005). Enzymatic diacylglycerol production has ever been studied by Watanabe *et al.* (2005) using fatty acid (FA) from soybean oil hydrolysis product. Huang *et al.* (2013) produced MDAG using Lipase GHI enzyme. Meanwhile, the use of glycerol in MDAG production can give a benefit because glycerol is the primary waste generated from biodiesel production (Adhitasari *et al.*, 2017; Colombo *et al.*, 2016).

As far as the literature survey being conducted, no report has been found on the use of cocoa based FFA in MDAG synthesis. This research presents the study of the esterification of glycerol with cocoa based FFA using calcium oxide catalyst derived from eggshell ash. This solid catalyst facilitates cheaper and easier product separation than the liquid catalyst (Colombo *et al.*, 2016; Niju *et al.*, 2014; Nuryoto *et al.*, 2017; Purba *et al.*, 2014; Tshizanga and Aransiola, 2017). Eggshell is abundantly available in Indonesia and it contains up to 66.16% calcium oxide. Therefore, it is a promising source of base catalyst (Nazar, 2013; Purba *et al.*, 2014).

The esterification reaction can be affected by some operating variables such as reaction time and temperature, the amount of calcium oxide as catalyst, and molar ratio of glycerol and FFA (Kombe *et al.*, 2013). The design of reactor for the esterification process requires the reaction kinetics data. Theoretically, esterification reaction of glycerol with FFA is a reversible reaction. This reaction can be shifted into an irreversible reaction if the products are immediately separated from the reaction system or when one of the reactant is in excess (Freedman, 1984; Narvaez, 2007; Rane *et al.*, 2016). In this research, molar ratio of glycerol with FFA was set to be very high so that the reaction can be assumed as an irreversible reaction. In addition, a chemical reaction which uses solid catalyst sized less than 840 µm, can be assumed to be a pseudo-homogeneous reaction (Joksimovic and Markovic, 2007). Based on the explanation above, this research has an aim to study the effects of reaction time and temperature on the esterification reaction conversion of glycerol with FFA into MDAG using calcium oxide catalyst and the reaction kinetics using a pseudo-homogeneous model approach. The reaction rate was assumed to follow either the first or second order kinetics as described in equation (1) and (2), where C = concentration, A = FFA (taken from the highest component, it is palmitic acid), r = reaction rate, *k* = Arrhenius' reaction rate constant, and t = time (Rane *et al.*, 2016).

$$-r_A = -\frac{dC_A}{dt} = kC_A^1 \tag{1}$$

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 \tag{2}$$

METHOD

Material

The FFA was obtained from BT COCOA, glycerol and tert-butanol used were obtained from chemical store in Semarang. While the calcium oxide used was obtained from calcinations of eggshell.

Method

The acid number, moisture content, and the components of FFA firstly analyzed. The composition of FFA was determined chromatographically a using gas chromatography mass spectrometry (GC-MS) system of Perkin Elmer GC-MS GC Claurus 680 - MS ClaurusSQ 8T. The operation conditions were as follows: instrument type was PE Autosystem GC, sampling rate was 1.5625, control of Carrier Flow-He, column length was 30 m, Split flow was 20 mL/minute, initial setpoint was 1 mL/minute, and diameter was 250 µm, oven temperature is programmed at 50-350°C, run time total was 13 minutes.

Prior to its preparation as catalyst, the eggshell was washed to remove dirt and dried to dryness. Then it was mashed and sieved using 340 mesh sieve. The calcium oxide content of eggshell was analyzed using atomic absorption spectroscopy (AAS). The AAS employed Analyse – 400 of Perkin Elmer with the operating conditions were wavelength at 283.3 nm, acetylene rate was 2.0 L/minute, the rate of air was 10.0 L/minute, slit width was 0.7 nm, and the height of burner was 2.0 nm.

A precisely weighed 40 g FFA waste was firstly heated to 105°C in a three-necks round bottom flask, before being mixed with fresh tert-butanol (3:1 v/w) (Anggoro, 2008) and heated to 60°C. Simultaneously, glycerol (6 times of the FFA moles) was also heated in beaker glass at 60°C prior to addition of 4% of w/w calcium oxide catalyst (Purba *et al.*, 2014). This mixture was then introduced into the three-necks round bottom flask and esterified under constant stirring at 400 rpm for 20 minutes. Samples were withdrawn at every 5 minutes interval. The sample was filtered to separate the calcium oxide from the filtrate containing MDAG, FFA, and glycerol mixture. The acids number of this filtrate was determined. A set of experiment were also conducted at different temperatures (70 and 80°C).

The reaction kinetics of esterification was derived from the mass balance of a pseudo-homogeneous model approach (Equations 1 and 2) and was done using curve-fitting method between conversion data and its count. Its reaction order was tested until it was obtained the order of reaction which produced the smallest average error. Arrhenius' reaction rate constants (*k*) of the resulted calculation for each temperature variables were used to find the values of collision factors (A) and activation energy (Ea) (Rane *et al.*, 2016).

RESULTS AND DISCUSSION

The chemical composition of the fatty acids from cocoa processing waste is shown in Table 1 and Figure 1.

Table 1. FFA compositions from waste of cocoa process using GC-MS analysis

Component	Concentration (%)
Palmitic acid	47.24
Methyl stearate	1.05
Oleic acid	25.39
Stearic acid	24.32

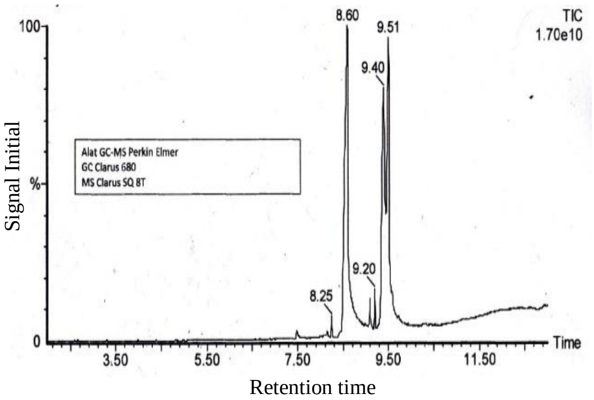

Figure 1. Result of chromatogram analysis of FFA from waste of cocoa process

The FFA from the cocoa processing waste are categorized into free fatty acids which can be used to produce MDAG through reaction with glycerol. The molecular weight of the FFA was then estimated based on the main component; which is palmitic acid (256.4241 g/mole). The acid number of the FFA from cocoa processing waste used in this research was 84.26%. This result is closely similar to that reported for palm oil, which is about 80% (Yustira *et al.*, 2016). The calcium oxide content in eggshell powder used in this research was about 24.01 mg/L. Some other animals also exhibit their potential as the source of calcium oxide as catalyst in coconut oil conversion into biodiesel (Nazar, 2013). Chicken's bones may contain calcium oxide as much as 56.28% (Mohadi *et al.*, 2013), whereas the shell of scallop provides 45% calcium oxide (Lestari and Hadiyanto, 2015).

The esterification of glycerol with FFA from cocoa processing waste using calcium oxide catalyst from eggshell produces high conversion of MDAG. Reaction conversion (x) is calculated from the derivation of FFA acidity, shown in equation (3). These conversion data are used to study the effects of its reaction time, temperature, and kinetics using homogeneous approach. The acid number and conversion of the reaction at various temperatures (60, 70, and 80°C) and reaction times are shown in Tables 2-4.

$$FFA\ Conversion = \frac{initial\ Acidity - Acidity\ t}{Acidity\ t}\ x\ 100\% \quad (3)$$

Table 2. Acid number and conversion of FFA on esterification of glycerol with FFA at 60°C using calcium oxide catalyst (initial weight of FFA is 40 g, ratio of FFA/Glycerol = 1:6 mole/mole, ratio of calcium oxide/FFA = 1:25 w/w)

Time (minutes)	Acid Number (%)	Conversion (%)
0	85.272	0.000
5	43.187	49.353
10	23.980	71.878
15	14.036	83.540
20	13.324	84.375
25	13.324	84.375
30	13.150	84.579

Table 3. Acid number and conversion of FFA on esterification of glycerol with FFA at 70°C using calcium oxide catalyst (initial weight of FFA is 40 g, ratio of FFA/Glycerol = 1:6 mole/mole, ratio of calcium oxide/FFA = 1:25 w/w)

Time (minutes)	Acid Number (%)	Conversion (%)
0	85.272	0.000
5	38.852	54.437
10	23.760	72.136
15	13.987	83.597
20	12.448	85.402
25	12.455	85.394
30	12.462	85.386

Table 4. Acid number and conversion of FFA on esterification of glycerol with FFA at 80°C using calcium oxide catalyst (initial weight of FFA is 40 g, ratio of FFA/Glycerol = 1:6 mole/mole, ratio of calcium oxide/FFA = 1:25 w/w)

Time (minutes)	Acidity (%)	Conversion (%)
0	85.272	0.000
5	39.469	53.714
10	23.651	72.264
15	13.710	83.922
20	13.181	84.543
25	12.455	85.394
30	11,871	86,078

As expected, the esterification reaction is affected by temperature. The conversion was higher at a higher temperature. In the beginning of the process, the effect of time on reaction conversion is very significant. It can be seen that at 5 minutes the conversion reaches 50%, whereas at 10 minutes the conversion can reach about 72%, and it is almost constant at the 20th minutes. Similar trend was reported by Rane *et al.* (2016). They found that at higher temperature (70, 90, and 110°C), the ratio of glycerol concentration and the initial concentration also rises from 0.98; 0.6; and 0.1 at 30 minutes, which corresponded to reaction conversions of 2, 40 and 90%, at 70, 90, and 110°C, respectively. That research used $SO_4^{2-}/\gamma\text{-}Al_2O_3$ catalyst. The conversion starts to be constant at 60 minutes at 110°C,

When the glycerol is used in excess, the esterification reaction of glycerol with FFA can be assumed to be an irreversible reaction (Freedman *et al.*, 1984). This idea is supported by Narvaez (2007) and Rane *et al.* (2016) who assumed that the value of *k* for the reverse reaction is assumed as zero when the glycerol is in excess. This esterification reaction used solid catalyst sized less than 840 µm, so that the reaction kinetics can be approached using the pseudo-homogeneous model (Joksimovic and Markovic, 2007). The kinetics of the reaction was determined by finding the most suitable reaction order. The first order reaction (Equation (1)) and its calculation can be calculated by using linearization of the graph between $-ln(1\text{-}x_A)$ as y-axis and t as x-axis, and its line must pass the (0,0). The value of reaction rate constant (*k*) is the same as the value of its line's gradient. Meanwhile, the second order reaction (Equation (2)) and it is calculated using the same method as the first order, the value of $x_A/(1\text{-}x_A)$ is as the y-axis and the value of t is as the x-axis. The value of *k* is the value of its gradient divided by the initial concentration of FFA (Levenspiel, 1999; Rane *et al.*, 2016). The initial concentration of FFA is calculated from the mass of FFA divided by the molecular weight and its solution volume (C_{A0} = 3.792 mole/L). Based on the calculation results, the value of reaction rate constants (*k*) using the first and second order approach are shown in Table 5.

Table 5. The values of reaction rate constant and average error of esterification of glycerol with FFA using calcium oxide catalyst (initial weight of FFA is 40 g, ratio of FFA/Glycerol = 1:6 mole/mole, ratio of calcium oxide/FFA = 1:25 w/w)

Temperature (°C)	Reation Rate Constant, k	Average Error (%)
1st Order Approach (k in 1/minute)		
60	0.1070	0.043
70	0.1086	0.051
80	0.1097	0.048
	Average Error	0.047
2ndOrder Approach (k in L/mole.minute)		
60	0.07384	0.028
70	0.07719	0.022
80	0.07938	0.021
	Average Error	0.024

In addition, the conversion data and its calculation results can be seen in Figures 2, 3, and 4 for temperature at 60, 70, and 80°C, respectively. The determination of kinetics model in this research is based on the value of average error from both models (Table 5).

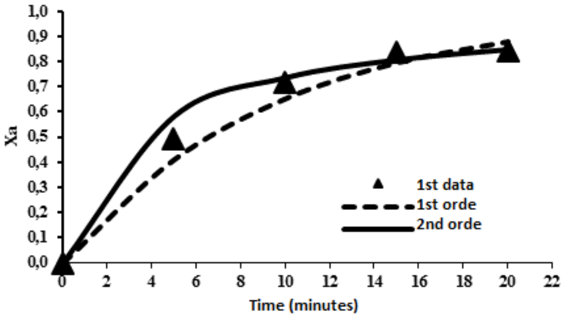

Figure 2. Comparison of data and calculation results of FFA conversion on esterification of glycerol with FFA using calcium oxide catalyst (initial weight of FFA is 40 g, ratio of FFA/Glycerol = 1:6 mole/mole, ratio of calcium oxide/FFA = 1:25 w/w) at 60°C

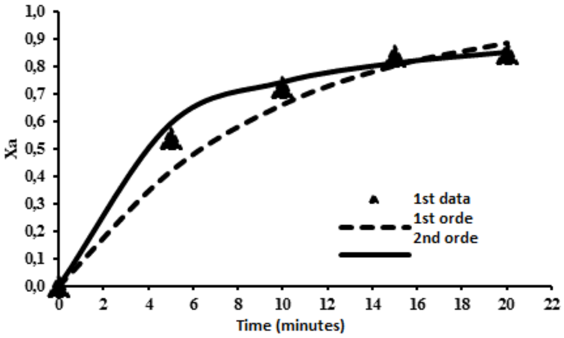

Figure 3. Comparison of data and calculation results of FFA conversion on esterification of glycerol with FFA using calcium oxide catalyst (initial weight of FFA is 40 g, ratio of FFA/Glycerol = 1:6 mole/mole, ratio of calcium oxide/FFA = 1:25 w/w) at 70°C

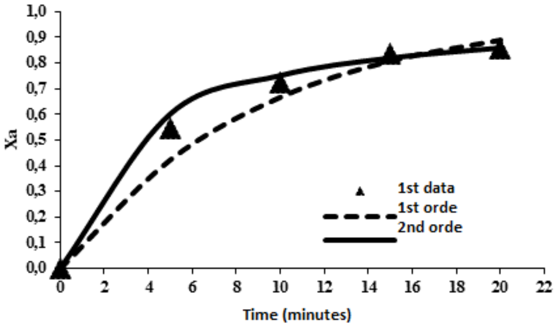

Figure 4. Comparison of data and calculation results of FFA conversion on esterification of glycerol with FFA using calcium oxide catalyst (initial weight of FFA is 40 g, ratio of FFA/Glycerol = 1:6 mole/mole, ratio of calcium oxide/FFA = 1:25 w/w) at 80°C.

Based on the Figures 2, 3 and 4, the second order kinetics model seems to be more appropriate to describe the reaction kinetics of esterification of glycerol with FFA than the first order kinetic approach. It can also be justified by lower value of average error of second order kinetics model. The *k* value of the first order kinetic model at 70°C was 0.1086 (1/minute). However, this *k* value is less than that reported by

Masduki *et al.* (2013), which is 0.31 (1/minute). This fact is likely to be affected by the difference of the catalyst used. The catalyst used in this research was calcium oxide, while the catalyst used by Masduki *et al.* (2013) was sulfated zirconia-zeolite catalyst. The latter catalyst was reported to have wider surface area than the former by which promoting a faster reaction rate. The *k* value at 70°C of the second order reaction in this research is 0.0772 (L/mole.minute). In the research of Rane *et al.* (2016), the *k* values were ranged from 1.99×10^{-7} to 1.194×10^{-5} (L/mole.minute). Therefore, the use of calcium oxide catalyst is better than $SO_4^{2-}/\gamma\text{-}Al_2O_3$.

Instead of affecting the conversion, temperature also affects the value of the reaction rate constant (*k*). Theoretically, the temperature and *k* can be correlated by the Arrhenius' equation (Fogler, 1999; Rane *et al.*, 2016). Accordingly, both the collision factor (A) and activation energy (Ea) of the Arrhenius equation can be evaluated. The values of *k* used in this calculation were those obtained from the second order model approach. The collision factor (*A*) and activation energy (*Ea*) can be obtained from the slope and intercept of the plot of 1/T versus ln *k* (Fogler, 1999; Rane *et al.*, 2016) shown in Figure 5. As a result, Arrhenius' parameters obtained is A = 0.2659 (L/mole.minute) and Ea = 3544 (J/mole).

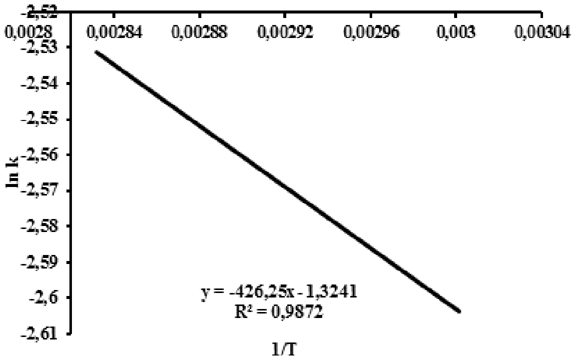

Figure 5. Relation between ln *k* and 1/T on esterification of glycerol with FFA using calcium oxide catalyst (initial weight of FFA is 40 g, ratio of FFA/Glycerol = 1:6 mole/mole, ratio of calcium oxide/FFA = 1:25 w/w)

CONCLUSION

Based on the research results, it can be concluded that the esterification reaction of glycerol with FFA using calcium oxide catalyst is affected by temperature and time. The higher temperature and the longer reaction time result in a higher reaction conversion. The second order reaction kinetics (average error of 0.024%) is more suitable model compared to first order. The effect of temperature on reaction rate constant follows the Arrhenius' function with the value of the collision factor (*A*) and activation energy (*Ea*) are 0.2659 (L/mole.minute) and 3544 J/mole, respectively.

ACKNOWLEDGEMENTS

The authors would like to thank Institute for Research and Community Services Universitas Negeri Semarang (LPPM UNNES) for financial support through Hibah Penelitian untuk Dosen 2016 with contract number of 1.11.7/PPK.4.5/2016.

REFERENCES

Adhitasari, A., Sulistyo, H., dan Prasetya, A., (2017), Sintesis Gliserol Karbonat dari Gliserol dan Urea Menggunakan Katalis Resin Indion 225 Na, *Reaktor*, 17, pp. 140-144.

Akoh, C.C. and Min, D.B., (2002), *Food Lipids-Chemistry, Nutrition, and Biotechnology*, Marcel Dekker Inc., New York.

Anggoro, D.D., (2008), Proses Gliserolisis Minyak Kelapa Sawit Menjadi Mono dan Diacyl Gliserol dengan Pelarut N-Butanol dan Katalis MgO, *Reaktor*, 12(1), pp. 22-28.

Colombo, K., Ender, L., and Barros, A.A.C., (2016), The Study of Biodiesel Production Using CaO as a Heterogeneous Catalytic Reaction, *Egyptian Journal of Petroleum*, 26, pp. 341-349.

Fogler, H., (1999), *Element of Chemical Reaction Engineering*, Prentice Hall Inc., New York.

Freedman, B., Pryde, E.H. and Mounts, T.L., (1984), Variables Affecting the Yields of Fatty Ester from Transesterifed Vegetables Oils, *Journal of American Oil Chemistry Society*, 60(10), pp. 1638-1643.

Hasenhuettl, G.L. in Hasenhuettl, G.L. and Hartel, R. W. (eds), (2008), *Synthesis and Commercial Preparation of Food Emulsifiers*, Springer Science, pp. 11-17.

Huang, J., Yang, Z., Guan, F., Zhang, S., Cui, D., Guan, G., and Li, Y., (2013), A Novel Mono- and Diacylglycerol Lipase Highly Expressed in *Pichia pastoris* and Its Application for Food Emulsifier Preparation, *Process Biochemistry*, 48, pp. 1899-1904.

Indarti, E., (2007), Efek Pemanasan terhadap Rendemen Lemak Proses Pengepresan Biji Kakao, *Jurnal Rekayasa Kimia dan Lingkungan*, 6(2), pp. 50-54.

Joksimovic, G. and Markovic, Z., (2007), Investigation of the Mechanism of Acidic Hydrolysis of Cellulose, *Acta Agriculture Serbia*, 12, pp. 51-57.

Kombe, G.G., Abraham, K.T., Hassan, M.R., Godwill, D.M., and Keat, T.L., (2013), Low Temperature Glycerolysis as a High FFA Pre-Treatment Method for Biodiesel Production, *Advances in Chemical Engineering and Science*, 3, p. 248.

Kurniasih, E., (2014), Sintesa Mono-Digliserida Melalui Reaksi Gliserolisis Enzimatis, *Jurnal Teknologi*, 14(1), pp. 25-28.

Lasisi, D., (2014), A Comparative Study of Effects of Drying Methods on Quality of Cocoa Beans. *International Journal of Engineering Research & Technology*, 3, pp. 991-996.

Lestari, S.P. dan Hadiyanto, (2015), Potensi Kerang sebagai Katalis untuk Pembuatan Biodiesel. *Prosiding Seminar Nasional Teknik Kimia "Kejuangan"-Pengembangan Teknologi Kimia untuk Pengolahan Sumber Daya Alam Indonesia*, UPN "Veteran", Yogyakarta.

Levenspiel, O., (1999), *Chemical Reaction Engineering*, Third Edition, Department of Chemical Engineering, Oregon State University, Corvallis, New York.

Masduki, Sutijan, dan Budiman, A., (2013), Kinetika Reaksi Esterifikasi Palm Fatty Acid Distilate (PFAD) menjadi Biodiesel dengan Katalis Zeolit-Zirkonia Tersulfatasi, *Jurnal Rekayasa Proses*, 7(2), pp. 59-64.

Mohadi, R., Lesbani, A., dan Susie, Y., (2013), Preparasi dan Karakterisasi Kalsium Oksida (CaO) dari Tulang Ayam, *Chemistry Progress*, 6(2), pp. 76-80.

Narv´aez, P.C., Rinc´on, S.M., and S´anchez, F.J., (2007), Kinetics of Palm Oil Methanolysis, *Journal of American Oil Chemistry Society*, 11(1), pp. 971-977.

Nazar, M., (2013), Pembuatan CaO dari Cangkang Telur Sebagai Katalis untuk Konversi Minyak Kelapa menjadi Biodiesel, *Prosiding Seminar Nasional dan Pendidikan Sains*, Prodi Pendidikan Kimia. UNSYIAH.

Niju, S., Begum, K.M.M.S., and Anantharaman, N., (2014), Modification of Egg Shell and Its Aplication in Biodiesel Production, *Journal of Saudi Chemical Society*, 18, pp. 702-706.

Purba, R.D.L., Nainggolan, M., dan Ritonga, M.Y., (2014), Pengaruh Rasio Pelarut Tert-Butanol Terhadap Minyak dan Suhu Reaksi Gliserolisis pada Pembuatan Mono dan Diasilgliserol (MDAG) Menggunakan Katalis Abu Cangkang Telur Ayam, *Jurnal Teknik Kimia USU*, 3(4), pp. 44-50.

Rane, S.A., Pudi, S.M., and Biswas, P., (2016), Esterification of Glycerol with Acetic Acid over Highly Active and Stable Alumina-based Catalysts: A Reaction Kinetics Study, *Chemical and Biochemical Engineering Quarterly*, 30(1), pp. 33-45.

Rumondang, I., (2016), Sintesis Monodiasilgliserol Berbasis Gliserol dan Palm Fatty Acid Distillate, *Jurnal Kimia dan Kemasan*, 38(1), pp. 1-6.

Setyaningsih, D., Bashir, B. Al., Silalahi, V.H.Y., and Muna, N., (2016), Purification of Mono-Diacylglycerol through Saponification and Solvent Extraction, *International Journal of Environment and Bioenergy*, 11, pp. 1-11.

Triana, R.N., (2014), Sintesis Mono dan Diasilgliserol (MDAG) dari Fully Hydrogenated Palm Kernel Oil (FHPKO) dengan Metode Gliserolisis, *Thesis*, Sekolah Pascasarjana, Institut Pertanian Bogor, Bogor.

Tshizanga, N. and Aransiola, E.F., (2017), Optimisation of Biodiesel Production from Waste Vegetable Oil and Eggshell Ash, *South African Journal of Chemical Engineering*, 23, pp. 145-156.

Wang, L., Wang, Y., Hu, C., Cao, Q., Yang, X., and Zhao, M., (2011), Preparation of Diacylgycerol-Enriched Oil from Free Fatty Acids using Lecitase Ultra-Catalyzed Esterification, *Journal of American Oil Chemistry Society*, 88, pp. 1557-1565.

Watanabe, T., Sugiura, M., Sato, M., Yamada, N., and Nakanishi, K., (2005), Diacylglycerol Production in a Packed Bed Bioreactor, *Process Biochemistry*, 40, pp. 637-643.

Yustira, Y., Rudiyansah, Alimuddin, A.H., Prawatya, Y. E., Wahyuni, N., dan Usman, T., (2016), Esterifikasi Asam Lemak dari Limbah Minyak Kelapa Sawit (Palm Sludge Oil) dengan Katalis Sn/Zeolit, *Prosiding Seminar Nasional II Penerapan Ilmu Pengetahuan dan Teknologi Universitas Tanjungpura*, Program Studi Kimia, Universitas Tanjungpura, Pontianak.