



## Synthesis of Glycerol Monooleate with MgO-Impregnated Natural Zeolite Catalyst

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### Abstract

Glycerol Monooleate (GMO) is synthesized via esterification, which involves the reaction between glycerol and oleic acid to yield monoglyceride esters. The esterification reaction is intrinsically slow, requiring the use of a catalyst to decrease the activation energy. The catalyst used in this study is a naturally occurring zeolite catalyst that has been altered through acid treatment and impregnation with  $Mg(NO_3)_2$ , and then subjected to calcination to convert it into MgO. Typically, this research consists of two steps: an initial phase where a natural zeolite catalyst is altered, followed by a subsequent phase where glycerol monooleate production. This study investigates the effects of different variables on the reaction. The variables include temperature (140–180°C), catalyst loading (3-10 %weight), glycerol to oleic acid ratio (2:1, 3:1, 4:1), reaction time (0–180 minutes), and stirring speed (125-525 rpm). The research results demonstrate that the highest conversion rate was achieved with a temperature of 180°C, a catalyst concentration of 10%, and a reactant ratio of 3:1 (glycerol to oleic acid). The ideal response time was found to be 120 minutes. The reaction kinetics can be estimated by employing a pseudo reaction equation that follows a first-order rate law. The rate constant, represented by  $k'$ , can be approximated using the Arrhenius equation. The reaction has an activation energy of  $-18.64 \text{ kJ.mol}^{-1}$ , and the value of  $A$  is  $1.41 \text{ cm}^3.\text{g}^{-1}.\text{minute}^{-1}$ .

**Keywords :** glycerol; oleic acid; glycerol monooleate; natural zeolite; esterification

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### INTRODUCTION

Mono fatty acid glycerides are a type of non-ionic surfactant that possess both hydrophilic and lipophilic properties. Mono fatty acid glycerides can be categorized into mono-saturated fatty acid glycerides and mono-unsaturated fatty acid glycerides based on the level of fatty acid saturation (Meng et al., 2023; Pal et al., 2019).. Monounsaturated fatty acid glycerides are more effective as emulsifiers compared to mono saturated fatty acid glycerides (Lee et al., 2018). Hence, there is significant interest in the development of glycerol monooleate (GMO) as an emulsifier due to its composition as an unsaturated fatty acid glyceride. GMO, or genetically modified organism, is a stable, light-yellow liquid that remains in a liquid state at room temperature. It possesses various properties such as emulsification, wetting, foaming, and anti-bacterial capabilities (Earnden et al., 2022).

The recent emergence of non-halal emulsifiers in various food products has raised significant concerns among society, particularly in Indonesia where most of the population is Muslim. GMO is an emulsifier product that is rumoured to be non-halal. GMO is an emulsifier derived from the chemical reaction between oleic acid and glycerol (Prasetyo et al., 2012). Oleic acid is derived from both animal fats and vegetable oils. Oleic acid is derived from animal fat, typically sourced from pork fat. Consequently, there has been extensive progress in the exploration of substitute sources for halal emulsifier raw materials. Therefore, vegetable oil-derived raw materials are more extensively utilized than animal fats in the production of halal emulsifier products.

Numerous studies have been conducted on the production of GMOs. Currently, the GMO manufacturing process continues to utilize homogeneous catalysts, including both acidic and basic solutions (Parhusip et al., 2012). One drawback of using homogeneous catalysts is the requirement for an additional purification process to separate the acid solution from GMO products. The residual acidic solution resulting from the separation process is typically unusable, or if it is intended for reuse, it necessitates a specialized handling procedure (Khorrami et al., 2012). Furthermore, the act of segregating the product and catalyst will generate environmentally detrimental waste due to the inability to recycle the leftover catalyst, necessitating more intricate waste management procedures. Additionally, the lingering catalyst present in the GMO product can pose a risk if it is combined with the food products that are consumed. Hence, the utilization of solid catalysts presents an intriguing alternative to homogeneous catalysts (Kurji & Abbas, 2023). A suitable solid catalyst is zeolite (Ramadhan et al., 2019; Setiadi et al., 2016). Zeolites can be classified into two categories based on their production: natural zeolites and synthesized zeolites. Natural zeolite is highly prevalent in Indonesia, especially in the region of Yogyakarta. Hence, further investigation into the application of natural zeolite is warranted. The utilization of catalysts derived from natural zeolites is gaining significant traction due to zeolites' inherent catalytic properties. Zeolite exhibits high thermal stability since its synthesis through GMO occurs at temperatures ranging from 160 to 300°C (Ferretti et al., 2010).

Hence, this study alters the properties of natural zeolite to enable its utilization as a catalyst in the production of GMOs. The objective of this study is to investigate the impact of reaction time, temperature, reactant ratio, catalyst loading, and stirring speed on the quantity of GMO generated (conversion of GMO). Meanwhile, to preserve its halal content, oleic acid derived from vegetable oil will be utilized as the raw material for oleic acid. Glycerol is a by-product of biodiesel production, making it both cost-effective and readily available (Putri et al., 2023).

## METHODS

### Materials

The materials utilized in this research comprise Oleic Acid, Glycerol, KOH from Merck, HCl 37% p.a. (Merck), NaOH (Merck),  $\text{Na}_2\text{S}_2\text{O}_3$  (Merck),  $\text{K}_2\text{Cr}_2\text{O}_7$  (Merck), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) p.a. (Merck),  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck), KI (Merck), Periodic acid ( $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ ) (Merck), Starch Paste, aquadest and Phenol Phtalein indicator. The zeolite used is Trembono zeolite stone, obtained from Gunung Kidul, and it is composed of zeolite (85%), plagioclase (10%), and volcanic glass (5%). The composition of zeolite is primarily comprised of mordenite (64% by weight) and clinoptilolite (23% by weight).

### Modification of Natural Zeolite

Resizing of natural zeolite to a particle size of - 60+80 mesh. Next, the zeolite was placed into a beaker and then 1 N  $\text{Mg}(\text{NO}_3)_2$  solution was added in a 3:1 ratio to the zeolite. The zeolite and  $\text{Mg}(\text{NO}_3)_2$  1 N solution was agitated using a magnetic stirrer for a duration of 60 minutes at a temperature of 80°C. Subsequently, the zeolite was isolated from the  $\text{Mg}(\text{NO}_3)_2$  1 N solution by means of filter paper. The procedure was iterated thrice. The zeolites were impregnated with  $\text{Mg}(\text{NO}_3)_2$  and then formed into a paste for subsequent calcination. The process of calcination was conducted at a temperature of 450°C for a duration of 8 hours.

### Synthesis of Glycerol Monooleate

Glycerol monooleate is synthesized through the reaction of glycerol and oleic acid. A solution containing glycerol, oleic acid, and a catalyst in specific proportions was introduced into a three-neck flask that was equipped with a condenser and a thermometer to monitor the temperature. The reactor was positioned on a magnetic stirrer that had a heater and a water bath with a temperature control. A specific quantity of oleic acid and catalyst were introduced into the reactor and heated to the desired reaction temperature with continuous stirring. Gradually, a volume of 125 mL of glycerol was introduced into the reactor. The temperature varied between 140 and 180 °C. The stirring velocity varied between 125 and 500 rpm. The mole ratio between glycerol and oleic acid used in this study varied at ratios of 1/1, 3/1, and 6/1. The catalyst employed exhibited variations ranging from 1 to 10% in terms of glycerol weight. The duration of the reaction time experiment ranged from 2 to 4 hours. After the reaction was completed, the catalyst was isolated from the reaction product through the process of vacuum filtration. The catalyst that had been separated was subsequently washed with n-

hexane (100 mL) and subjected to drying in an oven at 110°C for 24 hours to eliminate the n-hexane residue. The desiccated catalyst is capable of being reused for esterification reactions. The research was carried out by altering the temperature, catalyst percentage for activity testing, reaction time, and reactant mole ratio.

## RESULTS AND DISCUSSION

The research employs an esterification process to synthesize glycerol monooleate. The esterification reaction exhibits a notably sluggish rate, thus necessitating the addition of a catalyst to expedite the reaction (Groggins, 1958). The catalyst employed in this study is a heterogeneous catalyst in the shape of a natural zeolite catalyst. According to Setiadi et al. (2016), their research demonstrated that a zeolite catalyst functions as an ion exchanger, converting H<sup>+</sup> ions into cations. These cations then serve as initiators in the esterification reaction. During the initial stage of the reaction, electrons from the oxygen element in the oleic acid compound are transferred to H<sup>+</sup> ions located on the active side of the zeolite catalyst. This results in the formation of a carbon cation in the oleic acid compound. The carbon cation in oleic acid undergoes electron attack from the oxygen atom in the glycerol compound, resulting in a reaction between oleic acid and glycerol to produce glycerol monooleate.

### Effect of Reaction Time

Reaction time is a crucial factor that influences the resulting conversion. When the reaction time is extended, the conversion increases because there is a greater chance for collision between the reactant molecules (Parhusip et al., 2012). The research conducted by Meng et al. (2023) also elucidates that the conversion of oleic acid exhibits an upward trend as the reaction time is prolonged. Figure 1 displays the findings of this study. Figure 1 demonstrates a positive correlation between reaction time and the amount of oleic acid conversion. However, the duration of the increase is not sufficiently substantial. Figure 1 illustrates a notable increase in conversion up to 120 minutes, followed by a gradual decrease in the rate of increase beyond that point. The study determined that the ideal duration for the reaction between oleic acid and glycerol to form GMO is 120 minutes.

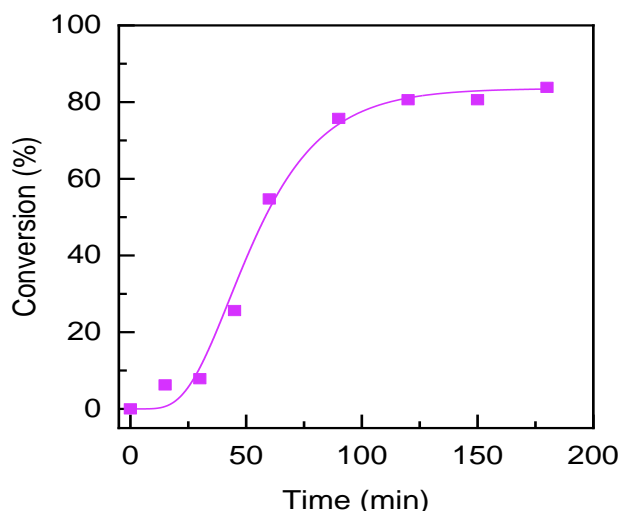
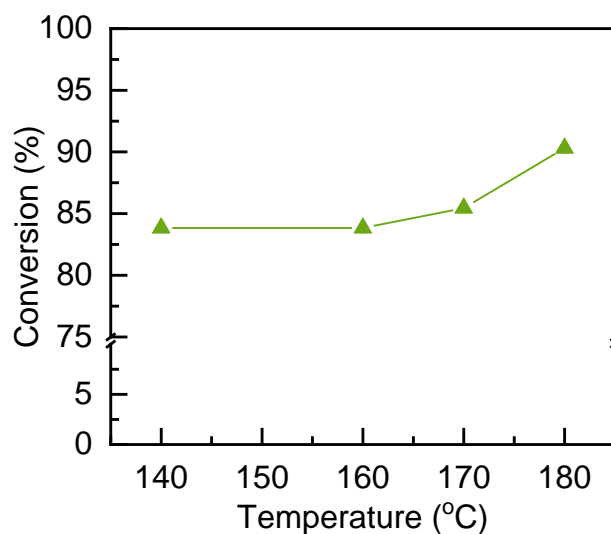


Figure 1. Conversion vs time

### Effect of Temperature

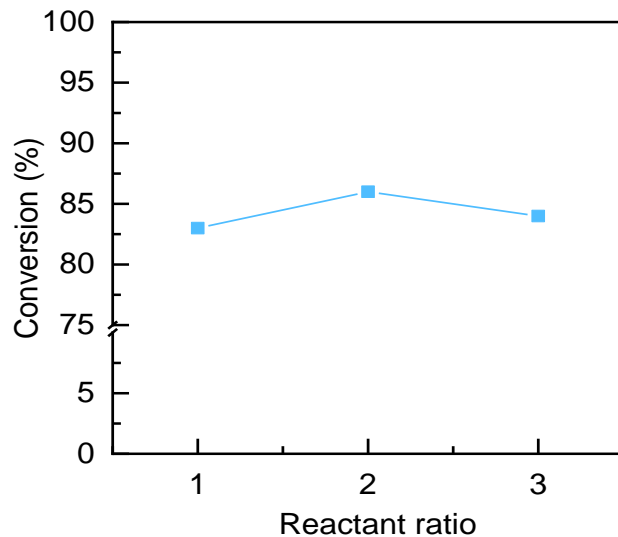
The esterification reaction of glycerol monooleate in this part was conducted in a stirred batch reactor with varying reaction temperatures of 140°C, 160°C, 170°C, and 180°C, using a glycerol to oleic acid ratio of 3:1. The stirring speed was set at 350 rpm for a duration of 3 hours. The esterification reaction in this study is exothermic due to the enthalpy change ( $\Delta H_R$ ) between glycerol and oleic acid being  $-\Delta H_R = -30 \text{ kJ} \cdot \text{mol}^{-1}$  (Kurji & Abbas, 2023). The conversion rate of oleic acid at various temperatures is presented in Figure 2. The conversion rate of oleic acid increases with temperature, resulting in an increase in the produced conversion, as stated by Putri et al. (2023) that an increase in operating temperature causes molecules to gain energy and move more effectively, leading to collisions that accelerate the reaction.



**Figure 2.** Conversion vs temperature

### Effect of Reactant Ratio

Esterification of glycerol monooleate is reversible. An excess of one of the reactants in an esterification reaction leads to a shift in the equilibrium towards the right and enhances the interaction between the reactants. The equilibrium position has a significant impact on the quantity of ester produced. By employing an excess amount of one reactant, the equilibrium can be shifted towards the product (Abd Razak et al., 2022; Mustafa et al., 2023). Thus, this investigation utilizes different proportions of glycerol to oleic acid, specifically 2:1, 3:1, and 4:1, carried out in a batch reactor with a stirring rate of 350 rpm at a temperature of 170 °C for a period of 3 hours.



**Figure 3.** Conversion vs reactant ratio

Figure 3 illustrates the extent to which the reactant ratio affects the conversion of oleic acid in glycerol monooleate esterification. The conversion rates for the reactant ratios of glycerol and oleic acid at 2:1, 3:1, and 4:1 is 83%, 85%, and 84%, respectively. The highest conversion was achieved at a glycerol: oleic acid reactant ratio of 3:1, with a yield of 85%. Nevertheless, the reactant ratios do not exhibit a substantial difference, and high ratios do not achieve an adequate conversion. This is feasible because of numerous variables, including an elevated reactant ratio.

### Effect of Catalyst Loading

The catalyst quantity was altered by 3%, 5%, 7%, and 10% by weight in relation to the glycerol: oleic acid ratio of 3:1. The stirring speed was set at 350 rpm for a duration of 3 hours. The esterification

reaction is characterized by a sluggish rate, necessitating the addition of a catalyst to expedite the reaction. Figure 4 demonstrates a positive correlation between the number of catalysts employed and the concentration of glycerol monooleate generated. This indicates that there is a correlation between the quantity of catalyst and the rate at which the reaction occurs (Abd Razak et al., 2022). An increase in the catalyst percentage will result in an acceleration of the reaction rate. The frequency of molecular collisions would increase if the reagent used is purer, thereby accelerating the reaction. Increasing the number of catalysts provides more opportunities for molecular collisions, resulting in higher reaction conversion rates at the same reaction time.

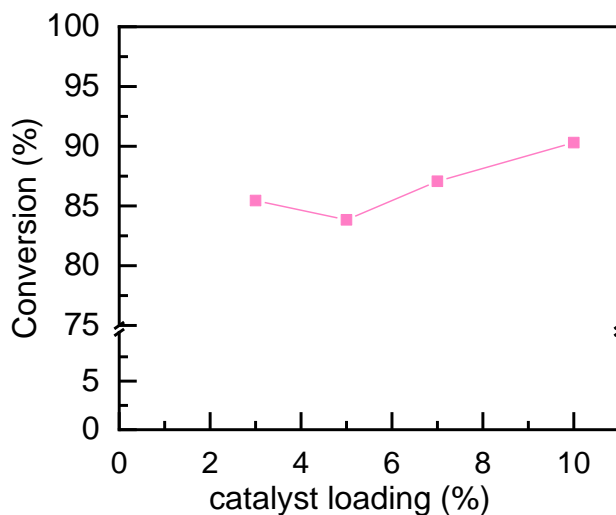


Figure 4. Conversion vs catalyst loading

#### Effect of Stirring Speed

The research involved conducting the reaction at an accelerated rate by utilizing a hot plate and employing a magnetic stirrer for agitation. The stirring speed was adjusted to 125 rpm, 240 rpm, 350 rpm, and 525 rpm. The purpose of stirring in the glycerol monooleate esterification reaction process is to optimize the reaction. Optimal stirring speed can rectify inadequate mixing between glycerol and oleic acid. Hence, the stirring velocity was altered in this investigation to determine the optimal stirring speed that would maximize the conversion of the reaction.

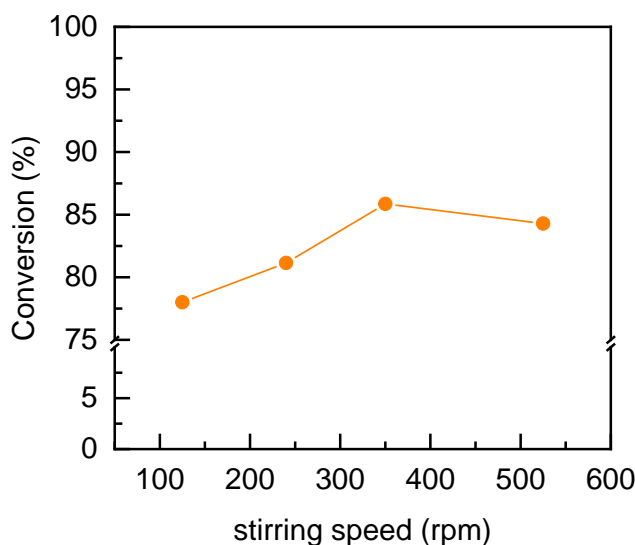


Figure 5. Conversion vs stirring speed

Experimental results in Figure 5 revealed that the conversion rate exhibited an upward trend from 125 rpm to 350 rpm, followed by a decline at a stirring speed of 525 rpm. The insufficient contact time between the material and solvent results in incomplete bonding before the stirrer's rotation speed

causes the bond to break again (Kurji & Abbas, 2023; Ramadhan et al., 2019)

**Kinetics of Reaction**

The expected result of the esterification reaction between glycerol and oleic acid in this study is the formation of glycerol monooleate. This occurs when a hydroxyl group (-OH) in glycerol is substituted with a fatty acid group. However, the reaction between glycerol and oleic acid occurs sequentially, resulting in the formation of additional products such as glycerol dioleate and glycerol trioleate. Thus, to achieve optimal production of glycerol monooleate, an excess amount of glycerol reactant is utilized to ensure complete conversion of oleic acid. The ideal ratio of glycerol to oleic acid produced in this study was 3:1. This research assumes that the reaction rate equation follows the format of a pseudo-homogeneous first order reaction. Equation 1 represents the mathematical expression for the reaction rate of the pseudo-homogeneous first order model.

$$(-r_{\text{oleic acid}}) = k' \cdot C_{\text{oleic acid}} \quad (1)$$

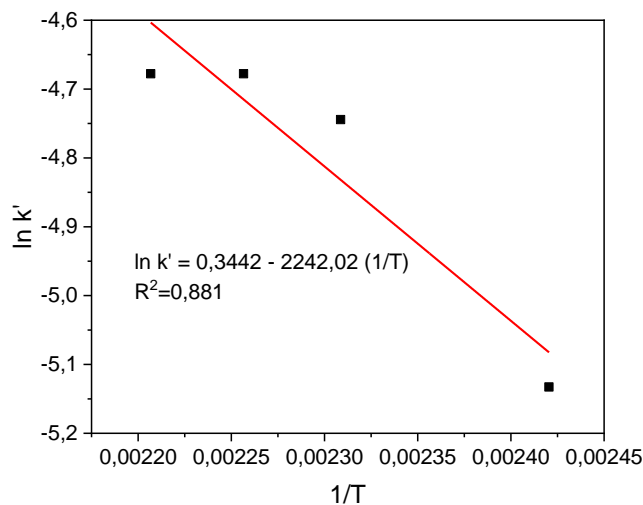
$(-r_{\text{oleic acid}})$  is the reaction rate of reducing oleic acid to GMO ( $\text{mol} \cdot \text{cm}^{-3} \cdot \text{min}^{-1}$ ).  $k'$  is the constant value of the chemical reaction rate ( $\text{cm}^3 \cdot \text{g}^{-1} \cdot \text{menit}^{-1}$ ) dan  $C_{\text{oleic acid}}$  is the concentration of oleic acid ( $\text{mol} \cdot \text{cm}^{-3}$ ). This equation can be solved using equation 2.

$$k' \cdot t = \ln \frac{C_{\text{oleic acid},0}}{C_{\text{oleic acid},t}} \quad (2)$$

$T$  is the duration of the reaction (min).  $C_{\text{oleic-acid},0}$  is the initial concentration of oleic acid ( $\text{mol} \cdot \text{cm}^{-3}$ ).  $C_{\text{oleic-acid},t}$  Oleic acid concentration at time  $t$  ( $\text{mol} \cdot \text{cm}^{-3}$ ). To solve Equation 2, a graph of  $\ln(C_{\text{oleat},0}/C_{\text{oleat},t})$  versus time can be generated for each temperature variation experiment. Then, each reaction temperature is assigned a  $k'$  value. The results of the calculation are demonstrated in Table 1. In order to ascertain the activation energy value of the reaction process for the formation of GMO from glycerol and oleic acid, calculations were conducted using the Arrhenius equation outlined in equation 3.

$$k' = A \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \quad (3)$$

$E_a$  is the activation energy of the reaction between glycerol and oleic acid to become GMO ( $\text{J} \cdot \text{mol}^{-1}$ ).  $A$  is the collision factor between particles ( $\text{cm}^3 \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ ).  $R$  is the ideal gas constant ( $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ).  $T$  is the reaction temperature (K). This equation can be solved by graphing the relationship  $\ln k'$  versus  $1/T$ . A graph of the relationship between  $\ln k'$  versus  $1/T$  is presented in Figure 6. From Figure 6, the values of  $E_a$  and  $A$  are obtained.



**Figure 6.** Ln k' vs (1/T)



**Table 1.** reaction rate constants, activation energy, and collision factors.

T, °C	k, cm <sup>3</sup> .g <sup>-1</sup> .min <sup>-1</sup>	Ea, kJ/mol	A, cm <sup>3</sup> .g <sup>-1</sup> .min <sup>-1</sup>
140	0.0059		
160	0.0087	18,64	1,41
170	0.0093		
180	0.0093		

## CONCLUSION

The reaction to produce glycerol monooleate from glycerol and oleic acid has been successfully executed using a natural zeolite catalyst impregnated with MgO. This research has revealed that the reaction to produce the GMO is influenced by the reaction time, temperature, catalyst concentration, reactant ratio, and stirring speed. The research findings indicate that the conversion rate will increase as the reaction time and temperature increase. The optimal reaction temperature is 180°C, and the optimal reaction time is 120 minutes. The conversion of oleic acid is also enhanced by an increase in catalyst concentration, with the highest concentration being achieved at a catalyst concentration of 10%. In contrast, the conversion of oleic acid did not exhibit any substantial differences because of changes in reactant ratios. And the stirring speed indicates that the conversion will increase as the stirring speed increases, and it will decrease if the stirring speed is excessive. The optimal stirring speed was achieved at 350 rpm.

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## REFERENCES

- Abd Razak, N. N., Cognet, P., Pérès, Y., Gew, L. T., & Aroua, M. K. (2022). Kinetics and hydrodynamics of *Candida antarctica* lipase-catalyzed synthesis of glycerol dioleate (GDO) in a continuous flow packed-bed millireactor. *Journal of Cleaner Production*, 373, 133816. <https://doi.org/https://doi.org/10.1016/j.jclepro.2022.133816>
- Earnden, L., Marangoni, A. G., Laredo, T., Stobbs, J., & Pensini, E. (2022). Self-Assembled glycerol monooleate demixes miscible liquids through selective hydrogen bonding to water. *Journal of Molecular Liquids*, 367, 120551. <https://doi.org/https://doi.org/10.1016/j.molliq.2022.120551>
- Ferretti, C. A., Soldano, A., Apesteguía, C. R., & Di Cosimo, J. I. (2010). Monoglyceride synthesis by glycerolysis of methyl oleate on solid acid-base catalysts. *Chemical Engineering Journal*, 161(3), 346–354. <https://doi.org/10.1016/j.cej.2009.07.041>
- Khorrani, S. A., Manuchehri, Q. S., & Sadeghipour, S. (2012). Surfactant-assisted Microwave Route to Fabricate CoFe<sub>2</sub>O<sub>4</sub> Nanoparticles. In *Hybd. Nanomat* (Vol. 1, Issue 3).
- Kurji, B. M., & Abbas, A. S. (2023). MCM-48 from rice husk ash as a novel heterogeneous catalyst for esterification of glycerol with oleic acid: Catalyst preparation, characterization, and activity. *Case Studies in Chemical and Environmental Engineering*, 8. <https://doi.org/10.1016/j.cscee.2023.100382>
- Lee, L. Y., Chin, N. L., Christensen, E. S., Lim, C. H., Yusof, Y. A., & Talib, R. A. (2018). Applications and effects of monoglycerides on frozen dessert stability. *LWT*, 97, 508–515. <https://doi.org/10.1016/j.lwt.2018.07.020>
- Meng, L., Shen, G., Zhang, S., Zhou, C., Han, Y., & Wen, R. (2023). New Technology for the Synthesis of Glycerol Monooleate. *Journal of Oleo Science*, 72(5), 549–556. <https://doi.org/10.5650/jos.ess22180>
- Mustafa, A., Ramadan, R., Niikura, F., Inayat, A., & Hafez, H. (2023). Highly selective synthesis of glyceryl monostearate via lipase catalyzed esterification of triple pressed stearic acid and glycerin. *Sustainable Energy Technologies and Assessments*, 57, 103200. <https://doi.org/https://doi.org/10.1016/j.seta.2023.103200>
- Pal, N., Samanta, K., & Mandal, A. (2019). A novel family of non-ionic gemini surfactants derived

- from sunflower oil: Synthesis, characterization and physicochemical evaluation. *Journal of Molecular Liquids*, 275, 638–653. <https://doi.org/10.1016/j.molliq.2018.11.111>
- Parhusip, R., Miskah, S., Raya Palembang Prabumulih Km, J., & Ogan Ilir, I. (2012). Pengaruh Waktu Reaksi dan Penambahan Katalis pada Pembuatan Gliserol Monooleat dari Gliserol dan Asam Oleat. In *Jurnal Teknik Kimia* (Vol. 18, Issue 1).
- Prasetyo, A. E., Widhi, A., & Widayat, D. (2012). Potensi Gliserol dalam Pembuatan Turunan Gliserol Melalui Proses Esterifikasi. *Jurnal Ilmu Lingkungan*, 10(1), 26–31. <http://ejournal.undip.ac.id/index.php/ilmulingkungan>
- Putri, D. I. M., Darmokoesoemo, H., Supriyanto, G., & Nugroho, N. A. (2023). Konversi Gliserol Menjadi Etanol dengan Mengintegrasikan Ultrasonik dan Katalis Ni/ZSM-5 Conversion of Glycerol to Ethanol by Integrating Ultrasonic and Ni/ZSM-5 Catalyst. *Eksergi*, 20(1), 1–7.
- Ramadhan, A. D., C.S, N. C., Nuryoto, N., & Kurniawan, T. (2019). The Use of Natural Zeolite as A Catalyst for Esterification Reaction Between Glycerol and Oleic Acid. *Reaktor*, 19(4), 172–179. <https://doi.org/10.14710/reaktor.19.4.172-179>
- Setiadi, F., Firmansyah, Ardiyani, R., Meilinda, A., & Rochmat A. (2016). Kinetika Reaksi Esterifikasi Gliserol Monooleat (GMO) Dengan Katalisator Zeolit Alam Bayah Teraktivasi Asam. *Jurnal Integrasi Proses*, 6(2), 73–82.