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SYNTHESIS OF OLEYL OLEATE WAX ESTER USING ACIDIC HETEROGENEOUS CATALYSTS

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ABSTRACT

Oleyl oleate wax ester one a liquid wax ester is predominantly used in biolubricants, plasticizers and cosmetics. This is due to their unique properties of being able to communicate wetting behavior at interfaces and show a non-greasy feeling when used on skin surfaces. Oleyl oleate was synthesized by the esterification reaction of oleic acid with oleyl alcohol in the presence of various acidic heterogeneous catalysts ($NaHSO_4$, $SnCl_2.2H_2O$ and NaH_2PO_4). The acidic heterogeneous catalyst of $NaHSO_4$ gave the highest percentage yield among the other catalysts used. $NaHSO_4$ showed the highest activity and achieved a higher yield. At the optimum condition, highest yield 96.8% of oleyl oleate was produced at 8 h of reaction time, the molar ratio of oleic acid to oleyl alcohol of 1:1, amount of catalyst of 9.9 wt% and at 130 °C reaction temperature. $NaHSO_4$ was best to be used as a catalyst and desiccant in the esterification reaction to produce oleyl oleate ester.

Keywords: Biolubricants, Oleyl Oleate Wax Ester, Esterification Reaction, Heterogeneous Catalysts
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INTRODUCTION

In fundamental wisdom, a lubricant is defined as a substance that can reduce friction between two solid metal surfaces rubbing against each other. Over the years, a great deal of effort has been devoted into the development of new lubricants with optimum qualities to meet the great increasing demands for a new generation of engines.[1,2] Always the impetus is the same; new innovations in machine design require new revolutions in lubricant composition. This development has led to an increase need for functional fluids that are biobased, biodegradable and low in toxicity. Typically, lubricants contain more than 80% base oil (most often petroleum-based fractions, called mineral oils) and less than 10% additives.[3] There are three classes in base oils: mineral oils (petroleum), plant oils and synthetic oils. Lubricants can be described in various categories, for example, engine oil, hydraulic oil and electric motor greases. Petroleum is the main base oil used in the production of lubricants. However, petroleum lubricants degrade less and harmful when released into the environment which has reinforced the incentive to provide biodegradable lubricants.[4]

Lubricants produced from plant oils are classified as good biolubricants due to their many advantages compared to petroleum oils. They are biobased, biodegradable, non-toxic to humans and other living organisms, no adverse effects on the environment and cheaper.[5] Other advantages include low volatility, good lubrication and a good anti-corrosion.[6,7] However, plant oil-based biolubricants occupy two major problems; insufficient oxidative stability and low fluidity at low temperatures.[8] For having many double bond fatty acids, the oil tends to be easily oxidized. At the same time, the fatty acids with a straight carbon chain decrease the pour point and result in poor low-temperature properties, which are obstacles to their utilization as bio-lubricant base oils. Either chemical modification of plant oils or synthetic ester production is required to address the problem.[9] Modifications by chemical processes may recover the thermal, oxidative and hydrolytic stability of the plant oils. The most important modifications occur in the unsaturation double bond and carboxyl groups of the fatty acids.[10] Synthetic esters improve two major drawbacks of biolubricants from plant oils that are, low oxidative stability and low-temperature properties. Oxidative stability can be improved by discarding the double bonds in the molecule as well as the absence of glycerol

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molecule, and reducing the structural uniformity through the production of branched ester improves the low performance at low temperatures.[11] Synthetic esters have other advantages: low volatility, as esters have strong dipole moment; lubricating well, as the polarity of the ester group will be attached to the surface of the metal; high stability against temperature, because the ester bond is stable and a few more. As one of the synthetic esters, wax esters have a notable advantage because of the configuration of dumbbells. The linear acid part contributes to a good viscosity index, while the branched alcohol produces a biolubricant with a low pour point.[12]

Wax esters are known as natural lubricating oils. Besides being used as natural lubricants like other ester types, wax esters can also be evaluated as synthetic biolubricating oils. In the field of the chemical modification of fatty acids to wax esters, the esterification of long fatty acids by various mono-alcohols including capryl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, lauryl alcohol and erucyl alcohol, have been generally described in the literature to produce their corresponding wax esters.[13-15] These wax esters are either fluid liquids or solid waxes. They are used as solvents in cosmetics or biolubricants in metal treatment, as well as the plastics and textile industries. The wax esters are generally produced by the esterification reaction of long fatty alcohol with long chain fatty acid in the presence of either homogeneous or heterogenous acid catalyst. The homogeneous catalyst used in traditional esterification is mainly sulphuric acid. Homogenous sulphuric acid cannot be reused and it has other disadvantages, such as more by-products, tedious workup procedure, equipment corrosion and environmental problems. Heterogeneous acid catalysts have concerned considerable consideration in recent years because of their significant advantages by removing many disadvantages elaborate with the use of homogeneous catalysts. These include like corrosion problems, separation of the pure product from the homogeneous catalyst, the generation of side products and posing environmental issue.[16-18]

The objective of this work was to test the catalytic ability of different acidic heterogeneous catalysts $NaHSO_4$, NaH_2PO_4, $SnCl_2.2H_2O$ for the esterification reaction of oleic acid with oleyl alcohol to produce oleyl oleate wax ester. The optimization of the esterification reaction through evaluation of several variables that affect the yield % of the product, such as the molar ratio of oleic acid to oleyl alcohol, amount of catalyst used, reaction time and reaction temperature.

EXPERIMENTAL

Materials

Oley alcohol (85%) and oleic acid (90%) were purchased from Aldrich Chemical Company (Germany). Acidic heterogeneous catalysts; sodium hydrogen sulphate ($NaHSO_4$), sodium hydrogen phosphate (NaH_2PO_4) and tin (II) chloride dehydrate ($SnCl_2.2H_2O$) were obtained from Fluka, Riedel-Dehaen and Aldrich, respectively. Sodium sulphate anhydrous (Na_2SO_4), sodium chloride (NaCl) and sodium hydrogen carbonate ($NaHCO_3$) were purchased from System Chemical Company. All the chemicals used in this study were either analytical or high-performance liquid chromatography (HPLC) grade and were used directly without further purification.

Synthesis of Oleyl Oleate using Acidic Heterogeneous Catalysts

The reaction was carried out in 100 mL three necks flask equipped with a condenser and magnetic stirrer, oleic acid (1 mole) was fed into the flask to preheat it before adding the acidic heterogeneous catalyst and the alcohol. When the desired reaction temperature (50, 70, 90, 110, 130, and 150 ˚C) was reached, the acidic heterogeneous catalyst (1.42, 4.2, 7.1, 9.9, 12.75 and 15.6 wt%) as a percentage of the weight of oleic acid and the oleyl alcohol (1, 2 and 3 moles) were placed into the flask and the reaction started. After completion of the reaction (2, 4, 6, 8, 10, and 12 h), the flask was allowed to cool to room temperature, and the crude product was dissolved using ethyl acetate 25ml and filtered to remove the acidic heterogeneous catalyst from the product. The product was transferred into a separating funnel and 10 ml of saturated $NaHCO_3$ solution was then added into the funnel to neutralize the acid catalyst used in the reaction. Brine (saturated NaCl) solution was then added to avoid the formation of an emulsion. Extraction was carried out until a solution with pH 7 was obtained, the aqueous layer was decanted and the product was dried with a sufficient amount of Na_2SO_4. The hydrated Na_2SO_4 was filtered off. Then, the product was rotary-evaporated to remove ethyl acetate at 77 ˚C, giving oleyl oleate as a viscous liquid.

Hammett Acidity Analysis

The acid strength of the catalyst was determined by the Hammett indicator technique. Before the analysis, 0.2 g of sample was treated under vacuum at 90˚C for 2 h, cooled to room temperature and contacted to the Hammett indicator 4-nitroaniline $pK(I)_{aq}$= 0.99 in distilled water to form 10mmol/L solutions. All the spectra were recorded with a Shimadzu UV-2450 UV-vis spectrophotometer. The acidic strength was determined by observing the cooler change of the indicator adsorbed on the surface of the sample. The change of color of the indicator shows that the acid strength of the sample is stronger than the indicator used. The acid strength is expressed by the Hammett acidity function, H_o, corresponding to the pKa of the indicator whereby the formula is shown in following equation:[19]

$$H_o = pKa\ (I)_{aq} + \log ([I]_s/[HI^+]_s) \quad (1)$$

RESULTS AND DISCUSSION

Effect of Acidic Heterogeneous Catalysts

To compare the catalyst activity employed in the esterification reaction, three different acidic heterogeneous catalysts were used: $NaHSO_4$, $SnCl_2.2H_2O$, and NaH_2PO_4. The operational conditions were; time of reaction was 2 h; temperature, 90 ºC; acid/alcohol molar ratio, 1:1; the amount of catalyst 4.2 wt% as a percentage of the weight of the oleic acid. Table-1 shows the results of the experiments carried out under the same conditions for comparing the catalytic performances of these three acidic heterogeneous catalysts.

Table-1: The Oleyl Oleate Ester Yield % based on the Acidic Heterogeneous Catalyst Used

Duration	Ester Yield (%)		
2 hr	NaH_2PO_4	$SnCl_2.2H_2O$	$NaHSO_4$
	38.00±2.28	41.67±1.65	51.37±2.07

Among those studied, $NaHSO_4$ seems to be the best choice; however, all the percentage yields achieved are low and not good for commercial purposes. This result may probably be due to the dependence of the esterification reaction on the acidity strength of the catalyst. To have a better explanation for this behavior the acidity of these three acidic heterogeneous catalysts was studied using the Hammett method. The acid strengths of these catalysts were evaluated from the determination of the Hammett acidity functions, using UV-visible spectroscopy. In the present case, this method consists of evaluating the protonation extent of the uncharged indicator base (named I) in solution, in terms of the measurable ratio $[I]/[IH^+]$. In a given solvent (S), assumed as being dissociating, the Hammett function (H_0) is defined in eqn.-1. As seen in Fig.-1 when the acidic heterogeneous catalyst was added, the absorption of the unprotonated form of indicator decreased. The absorbance of the unprotonated form of indicator on three acidic heterogeneous catalysts decreased as follows: NaH_2PO_4 >$SnCl_2.2H_2O$ > $NaHSO_4$.

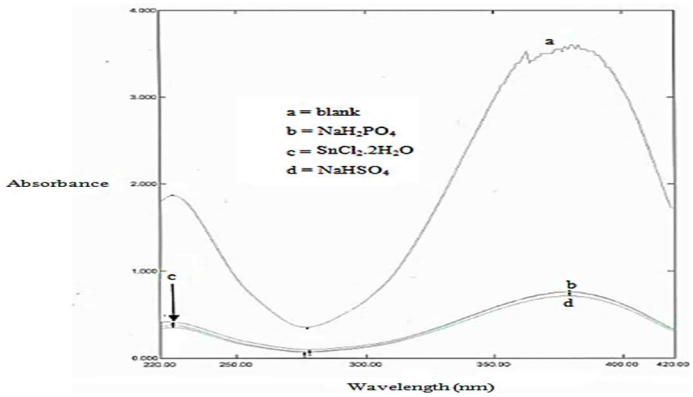

Fig.-1: Absorption Spectra of 4-nitroaniline for Acidic Heterogeneous Catalysts in Water

Table-2 shows the H_0 test occurred with 4-nitroaniline indicator solution. The absorption on the $NaHSO_4$ surface was lower and thus it has the smallest H_0. Therefore, the acidity of $NaHSO_4$ was higher compared to the acidity of $SnCl_2.2H_2O$ and NaH_2PO_4, respectively. The $NaHSO_4$ catalyst showed higher activity

among the acidic heterogeneous catalysts used, which can be attributed to the higher acid strength of $NaHSO_4$. Hence, the high % yield was achieved when using $NaHSO_4$ as a catalyst by lowering the activation energy of the esterification reaction of oleic acid with oleyl alcohol.[20]

Table-2: H_0 Values of Various Acidic Heterogeneous Catalysts [a]

Heterogeneous Catalysts	Absorbance [AU]	[I]%	[HI^+]%	H_0
4-Nitroaniline	3. 6	100	0	0
NaH_2PO_4	0.759	21.1	78.9	-0.573
$SnCl_2.2H_2O$	0.757	21	79	-0.575
$NaHSO_4$	0.714	19.8	80.2	-0.607

[a]Concentration: 10mmol/L

Effect of Reaction Time

Time course is a good sign for catalyst performance and reaction proceed. It can pinpoint the shortest or the adequate time important to get yields and minimize process expenses.[21] The effect of reaction time on the esterification reaction between oleic acid and oleyl alcohol is shown in Fig.-2. The reactions were performed within 2, 4, 6, 8, 10, 12 h and the other conditions of reaction were as follows: substrates molar ratio, 1:1; the amount of catalyst, 4.2 wt% as a percentage of the weight of the oleic acid; reaction temperature, 90 ˚C and $NaHSO_4$ catalyst. The % yield of oleyl oleate ester increased with the increasing time of reaction and gave a high percentage yield 84.32% within a reaction period of 8 h, whereas the percentage yield started to decrease with a reaction time of 10 h. This may be due to the production of the water molecule which had achieved the equilibrium state. Where producing water in the esterification reaction could lead the reaction go back towards the reactant. As the reaction proceeds, the substrates concentration decreases, which leads to a fall in the degree of saturation of the catalyst with the substrates.[22]

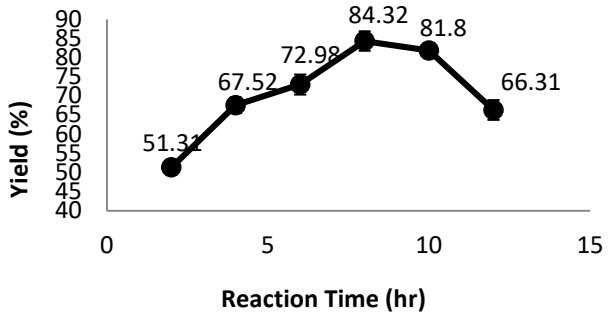

Fig.-2: Effect of Reaction Time on the Yield % of Oleyl Oleate

Effect of Mole Ratio of Substrates

The minimum mole ratio of substrates utilized is a challenge to meet the economic needs of any reaction. The effect of the molar ratio of oleic acid to oleyl alcohol on the esterification reaction is illustrated in Fig.-3. The other reaction conditions are as follows: reaction time, 8 h; the amount of catalyst, 4.2 wt% as a percentage of the weight of the oleic acid; reaction temperature, 90 ˚C and type of catalyst, $NaHSO_4$. The molar ratio of 1:1 (the oleic acid to the oleyl alcohol) yield 84.32% and decreased thereafter. The decrease yield % of oleyl oleate at high oleyl alcohol concentration 1:2 and 1:3 may be due to the oleyl alcohol present at very high concentration, and, thus, the viscosity of the liquid phase surrounding the catalyst molecule is increased leading to an ineffective mixing of reactants and reduction in reaction yield.[23]

Effect of Amount of Catalyst

From an application point of reaction, the amount of catalyst used should be as low as possible to obtain the desired result. Fig.-4 shows the % yield of oleyl oleate produced at different amounts of $NaHSO_4$ catalyst. The yield % of oleyl oleate ester increased with the increasing amount of catalyst and reached a maximum of 90.53% at 9.9% catalyst. This fact can be attributed to a higher number of molecules of substrate activated by the polarization of carbonyl, in presence of Na^+ catalyst. Thus, the nucleophilic attack by oleyl alcohol becomes more favorable and consequently, an increase on the formation of oleyl oleate was observed.[24] However, the yield % did not increase with the increasing amount of catalyst, and,

sometimes, it decreased the % yield of the product. Because water produced from the reaction has two negative effects, first towards the catalyst, where a fast interaction between the water and the catalyst might produce deactivation and thus reduce the rate of reaction and second towards the reaction itself. Since this is an equilibrium reaction the presence of the water produced could shift the reaction towards the reactant, and therefore achieve a lower final % yield of oleyl oleate.

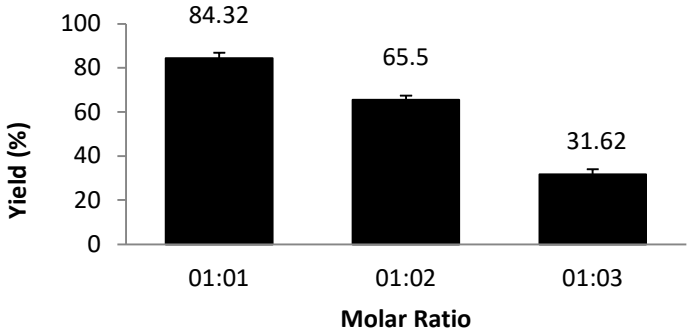

Fig.-3: Effect of Molar Ratio Oleic Acid and Oleyl Alcohol on the Yield % of Oleyl Oleate

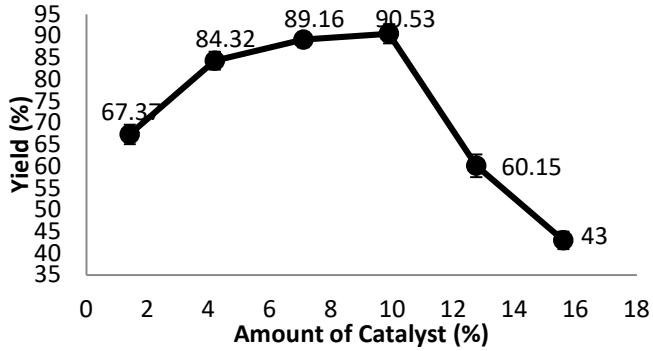

Fig.-4: Effect of Amount of Catalyst on the Percentage Yield of Oleyl Oleate

Effect of Reaction Temperature

Changes in the temperature of reaction affect the activity and stability of the catalyst, reactant solubility and thus the reaction rate. The esterification reaction of oleic acid with oleyl alcohol was carried out at six different reaction temperatures using $NaHSO_4$ as a catalyst. The yield % of ester at different temperatures is shown in Fig.-5.

The percentage yield of oleyl oleate increased with increasing temperature and the reaction temperature of 130 ºC produced the highest yield % of 96.81% compared to other reaction temperatures. This may be because at low temperatures the solubility is reduced with the sequence high viscosity causing mass transfer limitations, retarding reaction rate and lowering final yields, whereas, by increasing the reaction temperature, the reactant solubility improved in reducing the mass transfer limitation and making the reactant more available to the catalyst. In addition, the energy received from the higher temperature was utilized to increase the frequency of collision between the molecules.[22] Increasing the reaction temperature further decreased the yield % of oleyl oleate. This result may be due to the loss of catalyst activity at high temperatures. Since the esterification reaction is a reversal reaction, the amount of water producing from the reaction will influence the yield % of the product by forcing the reaction towards the reactants. Thus, it was appropriate to test the reaction by adding a quantity of desiccant to determine its effect on the ester yield %. In this step the esterification reaction of oleic acid with oleyl alcohol was performed using 50% wt% as a percentage of the weight of oleic acid silica gel under the following optimum reaction conditions: reaction time, 8 h; the amount of catalyst, 9.9 wt% as a percentage of the weight of the oleic acid; substrates molar ratio, 1:1 of oleic acid to oleyl alcohol and type of catalyst, $NaHSO_4$ at four different reaction temperatures. Fig.-6 shows the influence of the desiccant on the percentage yield of oleyl oleate.

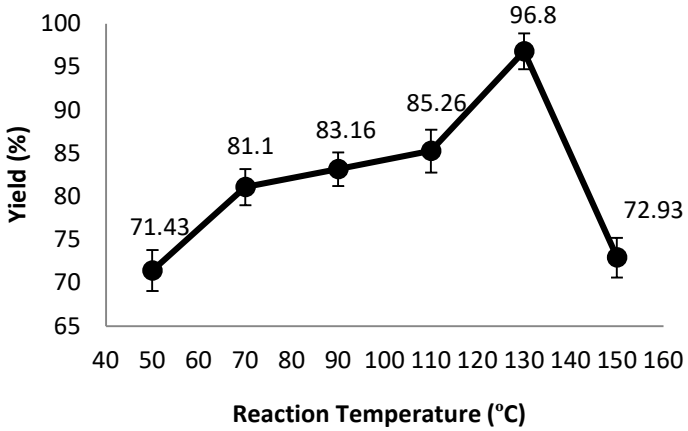

Fig.-5: Effect of Reaction Temperature on the Yield % of Oleyl Oleate

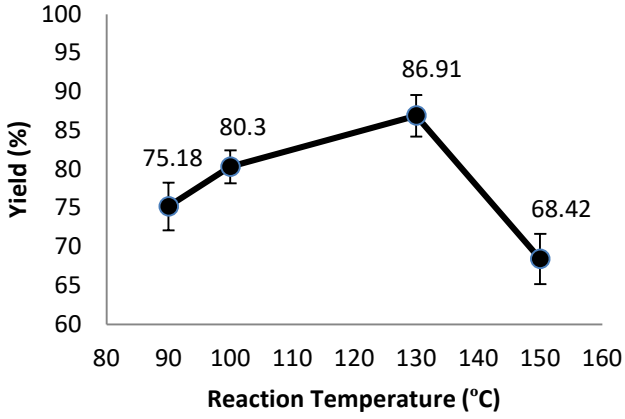

Fig.-6: Effect of Desiccant on the Yield % of Oleyl Oleate

Figure-6 shows that the highest yield % of oleyl oleate was achieved when the desiccant used was 86.91% at 130 ˚C. This result applies to the result obtained previously when the experiment was performed without the use of the desiccant, where the highest percentage yield of oleyl oleate was 96.8% at 130 ˚C. The equilibrium point in both cases did not change which indicates that $NaHSO_4$ has a dual function as a catalyst and a desiccant at the same time. Furthermore, the decrease in the yield % of oleyl oleate when using silica gel was due to the loss of the produced compound during the separation process of the silica gel from the reaction mixture using ethyl acetate as solvent.

CONCLUSION

Oleyl oleate was successfully synthesized by the esterification reaction of oleic acid with oleyl alcohol in the presence of various acidic heterogeneous catalysts $NaHSO_4$, $SnCl_2.2H_2O$ and NaH_2PO_4. $NaHSO_4$ shows the highest activity and achieved a higher final yield % due to its high acidity. Optimum conditions of the experiment to obtain high yield % of oleyl oleate were predicted at 8 hr of reaction time, the ratio of oleic acid to oleyl alcohol of 1:1, amount of catalyst: 9.9 wt% as a percentage of the weight of oleic acid and reaction temperature 130 °C. At the optimum condition, the yield % of oleyl oleate was 96.8%. $NaHSO_4$ was used as a catalyst and desiccant in the esterification reaction of oleic acid with oleyl alcohol. The low cost of the catalyst, easy separation from the product, its ability to absorb water, elimination of the catalyst preparation step and high yield % of oleyl oleate are the advantages of this process.

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REFERENCES

1. N.M. Nor, N. Salih and J. Salimon, *Asian Journal of Chemistry*, **33**(**1**), 67(2021), https://doi.org/10.14233/ajchem.2021.22938
2. Y.N. Lye, N. Salih and J. Salimon, *Applied Science and Engineering Progress*, **14**(**1**), **89**(2021), https://doi.org/10.14416/j.asep.2020.12.006
3. N.K. Attia, S.A. El-Mekkawi, O.A. Elardy and E.A. Abdelkader, *Fuel*, **271**, 117578(2020), https://doi.org/10.1016/j.fuel.2020.117578
4. W.A. Ahmed, N. Salih and J. Salimon, *Asian Journal Chemistry*, **33**(**6**) 1363(2021), https://doi.org/10.14233/ajchem.2021.23209
5. A.M. Bong, N.M. Kor, and P.T. Ndifon, *Green and Sustainable Chemistry*, **10**(**3**), 57(2020), https://doi.org/10.4236/gsc.2020.103005
6. M.N. Nurazira, N. Salih and J. Salimon, *Hemijska Industrija*, **75**(**2**), 117(2021), https://doi.org/10.2298/hemind200809009n
7. B. Murad, N. Salih and J. Salimon. *Applied Science and Engineering Progress*, **14**(**2**), 175(2021), https://doi.org/10.14416/j.asep.2021.03.004
8. J.A. Cecilia, D.B. Plata, R.M.A. Saboya, F.M.T. de Luna, C.L. Cavalcante and E. Rodríguez-Castellón, *Processes*, **8**(**3**), 257(2020), https://doi.org/10.3390/pr8030257
9. N. Salih and J. Salimon, *Biointerface Research in Applied Chemistry*, **11**(**5**), 13303(2021), https://doi.org/10.33263/briac115.1330313327
10. A. Özgülsün, F. Karaosmanôglu and M. Tüter, *Journal of the American Oil Chemists' Society*, **77(1)**, 105(2000), https://doi.org/10.1007/s11746-000-0017-5
11. N. Salih and J. Salimon, *Biointerface Research in Applied Chemistry*, **12**(**1**), 1185(2022), https://doi.org/10.33263/briac121.11851207
12. S. Teng, K.W. Khong and N.C. Ha, *Journal of Cleaner Production*, **274**, 122901(2020), https://doi.org/10.1016/j.jclepro.2020.122901
13. S. Sunitha, S. Kanjilal, P.S. Reddy and R.B.N. Prasad, *Tetrahedron Letters*, **48**(**39**), 6962(2007), https://doi.org/10.1016/j.tetlet.2007.07.159
14. K.M.W. Syamsul, M.R. Salina, S.O. Siti and M.N. Hanina, *World Applied Sciences Journal*, **11**(**4**), 401(2010).
15. M.B. Abdul Rahman, K.C. Yong, M. Basri, R.N.Z. Abdul Rahman, C.N.A. Razak and A.B. Salleh, *Malaysian Journal of Chemistry*, **3**(**1**), 46(2001).
16. P. Alpana and C. Uma, *Indian Journal of Chemical Technology*, **10**(**1**), 44(2003).
17. G.D. Yadav and M.B. Thathagar, *Reactive and Functional Polymers*, **52**(**2**), 99(2002), https://doi.org/10.1016/s1381-5148(02)00086-x
18. H.T.R. Teo and B. Saha. *Journal of Catalysis*, 228(1), 174(2004), https://doi.org/10.1016/j.jcat.2004.08.018
19. C. Thomazeau, H.O. Bourbigou, L. Magna, S. Luts and B. Gilbert, *Journal of the American Chemical Society*, **125**(**18**), 5264(2003), https://doi.org/10.1021/ja0297382
20. S. Shanmugam, B. Viswanathan and T.K. Varadarajan, *Journal of Molecular Catalysis A: Chemical*, **223**(**1-2**), 143(2004), https://doi.org/10.1016/j.molcata.2004.02.030
21. L.N. Yee, C.C. Akoh and S.G. Philips, *Journal of the American Oil Chemists' Society*, **74**(**3**), 255(1997), https://doi.org/10.1007/s11746-997-0132-y
22. J.B. Manley, P.T. Anastas and B.W.J. Gue, *Journal of Cleaner Production*, **16**(**6**), 743(2007), https://doi.org/10.1016/j.jclepro.2007.02.025
23. P.A. Claon and C.C. Akoh, *Journal of the American Oil Chemists' Society*, **71**(**6**), 575(1994), https://doi.org/10.1007/bf02540581
24. A.L. Cardoso, S.C.G. Neves and M.J. da Silva, *Energies*, **1**(**2**), 79(2008), https://doi.org/10.3390/en1020079

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