



Production of Oleic Acid Based Wax Ester Using Acidic Homogeneous Catalysts

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Abstract: Four homogeneous acidic catalysts were tested for their ability to catalyze the esterification reaction of oleic acid and oleyl alcohol to produce oleyl oleate, a wax ester. Sulfuric acid showed relatively higher specific activity. Various reaction parameters were optimised to obtain high percentage yield of oleyl oleate. The optimum condition to produce oeyl oleate was reaction time; 5 h, temperature; 90 °C, amount of sulforic acid 0.15 g and molar ratio of oleyl alcohol to oleic acid; 1:1. Percentage yield of wax ester obtained at these optimum reaction conditions was 93.88. Disappearance of carboxylic acid (C=O) peak has confirmed by FTIR with appearance of ester (C=O) peak at 1739 cm⁻¹. ¹H NMR spectra analyses confirmed the result of oleyl oleate with appearance of ester (-CH₂OCOR) at 4.02 ppm and also the ¹³C-NMR confirmed the result with appearance of ester (C=O) peak at 173.2 ppm. The low-temprtue behavior of compound synthesized was determined through its pour point (PP), viscosity index (VI) and flash point (FP) values. The results showed that oleyl oleate exhibited the most favorable low-temprtue performance of PP, VI and FP with -31 °C, 197.5 and 320 °C respectively. This is due to increase of the molacular weight thus improve the low temprtue property significantly.

Keywords: Wax ester, Oleic acid, Oleyl alcohol, Homogeneous catalyst, Esterification reaction

Introduction

Wax ester are an important class of fine organics that are widely used in cosmetic, pharmaceutical and lubricant industries¹. Special characteristics of non-toxicity, good fat soluble properties and excellent wetting behaviour at interfaces make them very special to be used in cosmetic formulations (cleansers, conditioners and moisturizers)². Natural wax ester can be extracted from animals and plant materials such as beeswax, sperm whale and jojoba oil. However, they are often in short supply and at present too expensive for commerical exploitation^{3,4}.

Wax esters are long chain esters that are derived from fatty acids and alcohols with chain lengths of 12 carbons or more⁵. Currently, most of the wax esters used commercially are of synthetic origin. They are generally produced by esterification reaction of an alcohol with an organic acid in the presence of an acid catalyst⁶. In order to start the esterification reaction, a proton transfer from acid catalyst to the alcohol and forms an alkylxonium ion. Acid is protonated on its carbonyl oxygen. Nucleophilic addition of a molecule of the alcohol to carbonyl carbon of acid forms an intermediate product. This intermediate product loses a water molecule and proton to give an ester⁷⁻¹¹.

Esterification reaction can be realized in the absence of catalysts, it is extremely slow, because of autoprotolysis of the carboxylic acid. Catalysts such as mineral acid, *p*-toluen sulphonic acid and ion exchange resins are always used in liquid phase esterification reactions to raise the product yield¹²⁻¹⁴. Since the naturally occurring wax esters are expensive and limited in access, the need to synthesize the compound has grown. There are many published papers using enzymatic catalysts to prepare oleyl oleate (wax ester). However there are no reported work using acid homogeneous catalyst for oleyl oleate synthesis.

Wax ester are usually harder, less greasy and more brittle than fats. The compounds have many potential applications due to their excellent wetting behavior at interfaces and a non-greasy feeling when applied on skin surfaces. Wax ester is also superior lubricant in high-speed machinery, work tools and metal cutters because it promotes extension of the life of all moving parts. Other examples of the commercial application of waxes are in detergent and polish used for the cleaning and protection of surfaces¹⁵. The physical properties of wax esters are very important from lubricant formulator point of view. Therefore the physical properties such as melting point, viscosity, specific gravity and reflective index were measured for pure wax ester. For example the melting points of long-chain wax esters (*e.g.* oleyl palmitate, oleyl oleate) are below 0 °C while the boiling points are up to 300 °C¹⁶.

The objective of this study was to synthesis wax ester by esterification reaction of oleic acid using homogeneous acid catalyst. Optimization the reaction with several variables that affect the yield such as molar ratio of oleic acid to oleyl alcohol, amount of catalyst, reaction time and reaction temperature have been done.

Experimental

Oleic acid (90%) and oleyl alcohol (85%) were purchased from Aldrich chemical company (Germany). Ethyl acetate, ethanol, sodium hydroxide, sodium hydrogen carbonate, *p*-toluene sulfonic acid, silica gel and sodium sulphate anhydrous were purchased from System Chemical company (Malaysia). Perchloric acid (70%) was obtained from aserate chemical company (Sydney). Sulfuric acid (96.7%) was purchased from J. T. Baker chemical company (USA). Phosphoric acid (98%) was obtained from BDH chemical company (UK). Filter paper was obtained from whatman (England).

In three necked flask equipped with a reflux condenser (0.0125 mol/ 3.6 g) of oleic acid was mixed with (0.0125 mol/ 3.53 g) of oleyl alcohol. The reaction mixture was heated on oil bath on a magnetic heater and stirrer until it reach the experiment temperature (90 °C); catalyst (0.004 mol/0.15 g) sulfuric acid and desiccant(1.8g silica gel) were added to the mixture at that moment.

After completion of the reaction, the flask was allowed to cool to room temperature and the crude product was washed with ethyl acetate (3 times 25 mL) and filtered to remove the silica gel from the product. The product was transferred into separating funnel and 10 mL of saturated NaHCO₃ solution was then added into the funnel to neutralize the catalytic inorganic acid used in the reaction. Brine (saturated NaCl) solution was then added in order to avoid any emulsion formation.

Extraction was carried out until getting solution with pH 7, the aqueous layer was decanted and the product was dried with sufficient amount of Na_2SO_4 . The hydrated Na_2SO_4 was filtered off. The dried product was then passed through a column packed with silica gel to remove any coloured or decomposed materials formed during the reaction. The columned product was rotary-evaporated to remove the solvent.

Dectection tests for evaporated compound has been done by using fourier transformation infra-red (FTIR), carbon and proton nuclear magnetic resonance (^{13}C NMR and ^1H NMR) in order to detect the carbonyl group for oleyl oleate

Viscosity index (VI) of the suntheized compound was determined using rheometer with model physical MCR 301 from anton paar instruments company (Germany), while measurements had run on hot plate heater set at 40 °C and 100 °C. Some physical properties such as pour point (PP), flash point (FP) and viscosity index have been calculated using different procedures¹⁷.

Results and Discussion

Figure 1 demonstrate the scheme for the esterification of oleyl oleate reaction. The esterification reaction was carried out with four different kind of homogeneous catalyst such as sulfuric acid, phosphoric acid, *p*-toluene sulfonic acid and perchloric acid at the same reaction conditions. The ester yield % of every reaction were investigated and compared with each other. Initial esterification conditions were choosen accoording to the study by Aksoy *et al.*¹⁸ duration, 1 h; temperature, 90 °C; acid/alcohol molar ratio, 1:1; type of catalyst, sulfuric acid; amount of catalyst 1.25% of the weight of the oleic acid; desiccant, silica gel (powder); amount of desiccant, 50% of the weight of the oleic acid. The comparison of ester yield value is shown in Table 1. The highest percentage yield was observed in experiment with sulfuric acid because of it increase the reaction rate at the esterification process, which the H_2SO_4 is insensitive to the presence of FAA in the feedstock¹⁹ the ester yields in the experiment with perchloric acid and phosphoric acid were similar, whereas the yield in the presence of *p*-toluene sulfonic acid higher than with phosphoric and perchloric acid may be due to formation of reagent-catalyst hydrogen bonds²⁰.

In the experiments with phosphoric acid, perchloric acid and *p*-toluene sulfonic acid the products where oily, but after a period of time the product had turned into semisolid. This behavior was not observed in the product in which sulfuric acid was catalyst.

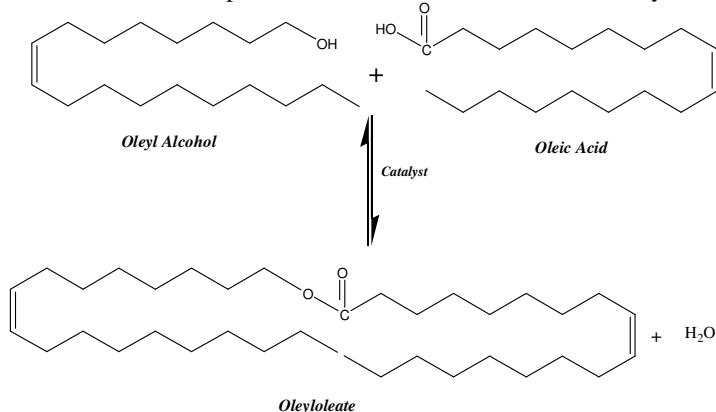


Figure 1. Synthesis of oleyoleate

Table 1. Comparison of the esterification yields in reactions using various catalysts

Duration 2 h	Ester yield, %			
	Sulfuric acid 93.88	Phosphoric acid 52.7	Perchloric acid 54.9	p-TSA 70

The effect of mole ratio of oleic acid: oleyl alcohol and the yield obtained are shown in Figure (2). The highest percentage yield of wax ester achieved was 93.88% with oleic acid to oleyl alcohol mole ratio of 1:1 in 5 h. Furthermore, increase of this mole ratio did not increase in the percentage yield of wax ester. This non-common behavior is due to dissolution *vs.* kinetics effect. For short times, when the amount of alcohol is high, a dissolution effect of the alcohol over the reaction mixture takes place with a stronger influence than that provided by the kinetics, producing a smaller reaction rate²¹. Furthermore, this result probably due to the hindered the interaction between oleic acid and catalyst with excess alcohol. This was reported earlier by Abdul Rahman *et al.*²².

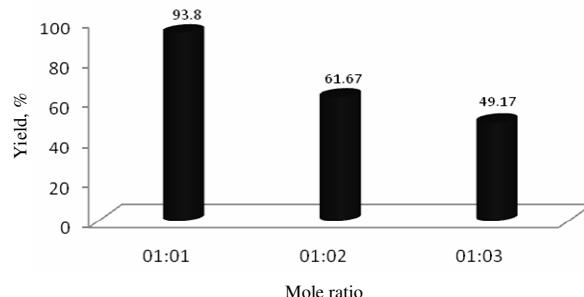
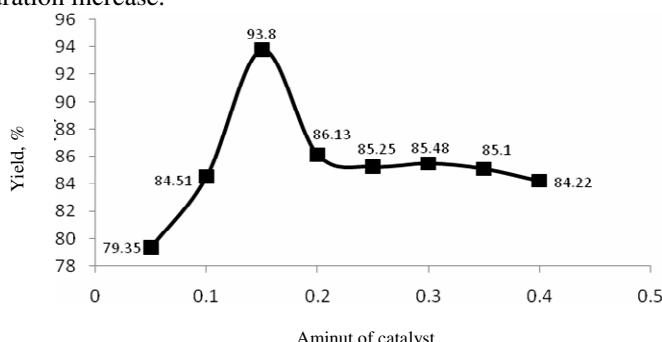
**Figure 2.** Effect of molar ratio on the esterification reaction of oleic acid and oleyl alcohol

Figure (3). Shows the effect amount of sulfuric acid on the esterification reaction. The percentage yield of wax ester increased with increasing amount of sulfuric acid 0.15 g to reach maximum value of 93.88%. Nevertheless, when the experiment was repeated with 0.20 g of sulfuric acid the percentage yield decreased, which this based on equilibrium concept²². This phenomenon could be due to the catalyst becoming less active when the extent of hydration increase.

**Figure 3.** Effect of amount of catalyst on the esterification reaction of oleic acid and oleyl alcohol

The effect of reaction time on oleic acid conversion is shown in Figure (4). Esterification yield increased with increasing the reaction time reaching maximum of 93.88% in 5 h at 90 °C, whereas the percentage of yield started to decrease with reaction time 6 h. Finally, the

ester yield value did not increase when the reaction time was prolonged. This is due to the reaction has achieved the equilibrium state where the rate of forward reaction is equal to the rate of backward reaction, hence the concentration of the product was unchanged²³.

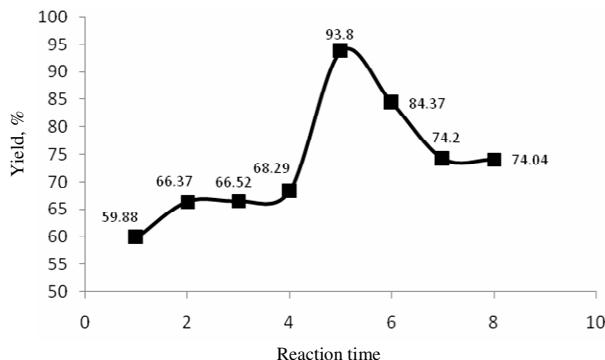


Figure 4. Effect of reaction time on the esterification reaction of oleic acid and oleyl alcohol

The effect of reaction temperature on the percentage yield of wax ester is shown in Figure 5. The percentage yield increased with arise in temperature, reaching a maximum of 93.80% in 5 h at 90 °C. While the reaction was carried out using reaction temperature up to 90 °C, the the percentage yield decreased with reaching a minimum of 74.77% at 130 °C. Based on the above experiments 90 °C was found to be the most stable reaction temperature because of the ester percentage yield and consumption of energy²⁴. This result corroborate those obtained by (Abdul Rahman & Aracil *et al*)^{22,25}, which happened due to reduce of the catalyst affectivity by heat at high temperature²².

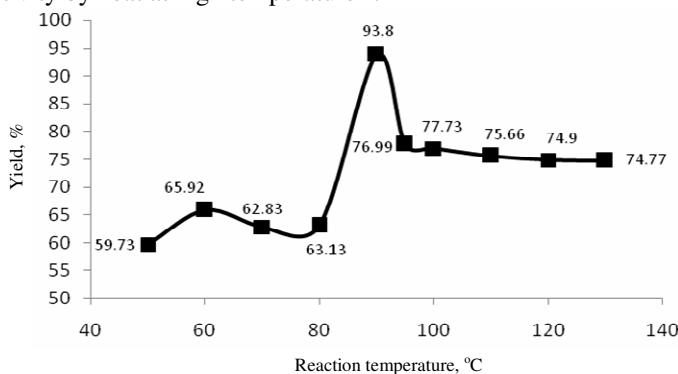


Figure 5. Effect of reaction temperature on the esterification reaction of oleic acid and oleyl alcohol

In order to prove the present of C=O of wax ester (oleyl oleate), the final product was tested by FTIR, ¹³C and ¹H. The comparison between oleyl alcohol, oleic acid and oleyl oleate FTIR spectra is shown in Figure 6. The date of ¹³C-NMR and ¹H-NMR spectra is shown in Table 2 & 3. C=O group of wax ester can be detected at wave- number 1735-1750 cm⁻¹, while stretching vibration peak of =CH at 3000-3050 cm⁻¹, stretching vibration peak of free OH for alcohol can be detected²⁶ of wavenumber 3300-3400 cm⁻¹. Based on Figure 6. FTIR spectrum of wax ester show stretching vibration peak at wavenumber 1739 cm⁻¹ attributed to carbonyl stretching frequency of ester moiety. This band combined with two C-O stretching

bands one stronger and broader than other were occurred in the rang 1172 and 1353 cm^{-1} , respectively. Whereas, the absorption due to OH of hydroxyl group 3338.38 cm^{-1} and carbonyl group of carboxylic acid at 1709.87 cm^{-1} are not observed which confirmed that the esterification reaction was taken place. Based on Table 1 and 2, the presents of C=O wax ester can be confirmed by comparison with previous study by Awang *et al.*²⁷ ^{13}C and ^1H chemical shift ranges (ppm). ^{13}C chemical shift ranges for unsaturated bond was 100-150 ppm, while for C-O was 40-80 ppm, whereas ^{13}C chemical shift value for C=O ester was 155-185 ppm. ^1H chemical shift ranges for aliphatic protons, normally at about 1.25-2.53 ppm which would also be shifted down field²⁸. However, the methine proton signal was shifted upfield at about 4.60-5.30 ppm which indicates the presence of this type of proton²⁹. Furthermore, the most important feature for success of esterification reaction is the presence of the COOCH₂ signal at about 4.02 ppm.

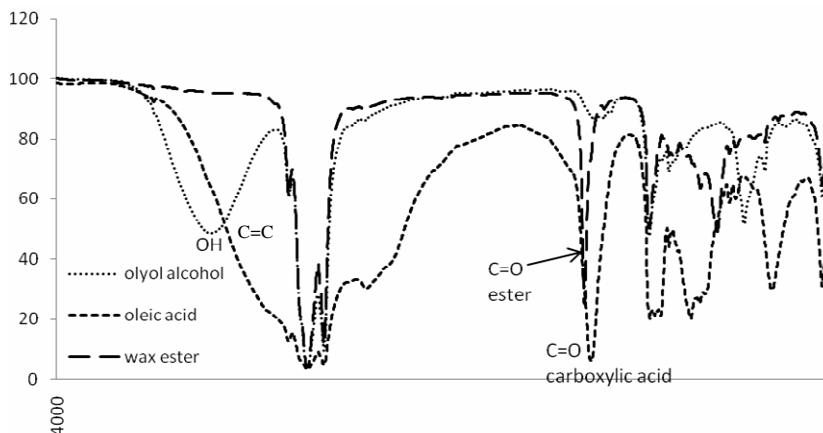


Figure 6. The FTIR spectra of oleyl oleate, oleic acid and oleyl alcohol

Table 2. The main signals present in ^{13}C -NMR functional groups of oleyl oleate

Assignment	Chemical shifts, ppm	Chemical shift, ppm ²⁷
C=O	173.2	173.2
C=C	130.6	131.0
C-O	64.59	65.9
CH ₂ -COO-CH ₂	32.82 22.76-29.98	33.5 22.5-30.1
CH ₃	14.12	14.5

Table 3. The main signals present in ^1H -NMR functional groups of oleyl oleate

Assignment	Chemical shifts, ppm	Chemical shift, ppm ²⁷
-CH ₂ -COO	2.26	2.25
-CH=CH-	5.32	5.43
CH ₂ -O-CO	4.02	4.08
C=C-C-H	1.85	1.96
CH ₂	1.23-1.33	1.29-1.33
CH ₃	0.85	0.96

Physicochemical properties of prepared compounds are summarized in Table 4. It is known that, as the chain length of the chain ester is increased, corresponding improvement in low temperature behavior was observed. This is due to the greater ability of the longer chain ester which more effectively disrupts crystalline formation at reduced temperature. Therefore, the liquid compound in this study was screened for cold flow performance through the determination of pour point. Another important factor in determining how well oil will behave as a potential biolubricant is to evaluate the oil flash point³⁰. The flash point is often used as a descriptive characteristic of oil fuel and it is also used to describe oils that are not normally used as fuels. There are various international standards for defining each, but most agree that oils with a flash point less than 43 are flammable, while those having a flash point above this temperature are combustible³¹. The efficiency of the biolubricant in reducing friction and wear is greatly influenced by its viscosity, the viscosity of oils decreases as temperature increases. If the biolubricant is too viscous, it will require a large amount of energy to move; if it is too thin, the surfaces will rub and friction will increase. The viscosity index highlights how a biolubricant's viscosity changes with variations in temperature. The best oils (with the highest VI) will not vary much in viscosity over such a temperature range and therefore will perform well throughout. In this work, increased viscosity index (VI) of the prepared product is the result of its higher molar weight and especially the altered structure of its molecule (Table 4).

Table 4. Physical properties of oleylolate ester

Pour point, °C	Flash point, °C	Vis.@40°C(cSt)	Vis.@100°C(cSt)	Vis index
-31	320	17.80	5.35	197.5

Conclusion

The sulfuric acid catalyst has been chosen as a higher activity on the esterification of oleic acid with oleyl alcohol. The reaction about 93.88% under optimal reaction conditions which were determined to be as follow: duration, 5 h; temperature, 90 °C; acid/alcohol molar ratio, 1:1; type of catalyst, sulfuric acid; amount of catalyst, 4.1% of the weight of acid.

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