



Synthesis and physical characterization of oleyl oleate using acidic heterogeneous catalyst sodium hydrogen sulfate NaHSO_4

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Highlights

- Optimization reaction of oleyl alcohol with oleic acid using heterogeneous sodium hydrogen sulfate can produce high yield of oleyl oleate wax ester at 1:1 molar ratio of substrates, 10% catalyst amount, 130 °C and 8 h.
- Physical characterization of oleyl oleate wax ester was achieved, (FTIR) 1739 cm^{-1} , (H-NMR) 4.02 ppm of COOCH_2 , (C-NMR) 40-80 ppm of C-O group and 155-185 ppm of carbonyl ester.

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ABSTRACT

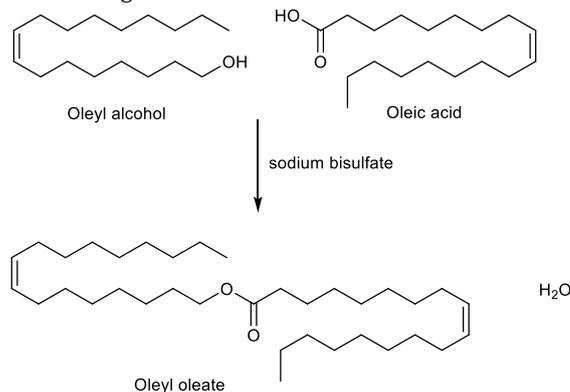
The esterification of oleic acid with oleyl alcohol under mild conditions and without any additional organic solvent was studied. High yield (90%) is obtained at optimized conditions 8 h, 130 °C and catalytic amount NaHSO_4 (10%). Analysis of the product of the reaction using FTIR, ^1H and ^{13}C -NMR showed the presence of oleyl oleate.

1. Introduction

Wax ester can be defined as high molecular weight esters that are derived from long chain fatty acids and alcohols, which are widely used in biolubricant industries, cosmetic, and pharmaceutical (Brett *et al.*, 2013; Parmita, 2016). Wax esters can be constituted by saturated ester can come from bee wax, whereas, unsaturated or liquid wax esters from the sperm whale and jojoba oil. However, they are often too expensive (Prapulla *et al.* 1992; Langrand *et al.*, 1988). Presently, most of the wax esters are used of synthetic origin. Generally, they are prepared by esterification of an alcohol with an organic acid using homogeneous catalyst. The traditional esterification used a homogeneous acid catalyst, sulfuric acid which cannot be reused and cause equipment corrosion and environmental problem. p-toluene sulfonic acid is higher cost, difficult separation and more consumption of energy. Heterogeneous acid catalysts are considered because of their significant advantages of eliminating many of the disadvantages involved with the use of homogeneous catalyst like the generation of side products, posing environmental, corrosion problems and separation of pure product from the homogeneous catalyst (Altiokka and Citak, 2003; Teo and Saha, 2004).

Several research efforts have also been performed to produce oleyl oleate ester using enzymatic and homogeneous catalysts. Where Abdul Rahman and co-worker were synthesized oleyl oleate ester using lipozyme as catalyst with percentage yield 90% (Abdul Rahman *et al.*, 2001), while $\geq 90\%$ of oleyl oleate ester was obtained in presence of immobilised lipase from candida antartica as catalyst by Radzi *et al.* (2005). Further, p-toluene sulfonic acid was used to prepare oleyl oleate ester with high conversion of 100% of

oleic acid into ester in a short time of 100 min (Sayed and Yutaka, 2000). In recent years, sodium hydrogen sulfate has gained much interest in the synthesis of octahydroxanthenes (Das *et al.*, 2007), protection and deprotection, nitration (Zolfigol *et al.*, 2001), nitrosation oxidation (Shirini *et al.*, 2005), synthesis of halide derivatives, coupling of indoles (Ramesh *et al.*, 2003), synthesis of quinazolinones and esterification. Herein, we describe a new, simple and effective procedure for the one-pot synthesis of oleyl oleate wax ester via oleic acid and oleyl alcohol esterification with sodium hydrogen sulfate as catalyst (Scheme 1). The catalytic ability of acidic heterogeneous sodium bisulfate NaHSO_4 catalyst for ester synthesis is tested. The effects of different parameters were investigated. Thus, the synthesis of synthetic liquid wax ester has the potential of meeting the demand of these esters.



Scheme 1. Synthesis of oleyl oleate

2. Experimental

Materials: Oleic acid (90%), oleyl alcohol (85%), Sodium bisulfate from Aldrich Chemical Company (Germany). Ethyl acetate, and sodium sulphate anhydrous, sodium chloride, sodium hydroxide, sodium hydrogen carbonate were purchased from System Chemical Company (Malaysia). Filter paper was obtained from Whatman (England). Synthesis of oleyl oleate: oleyl alcohol (0.0125 mol/3.53 g) was added to oleic acid (0.0125 mol/3.6 g) in three-necked round bottom flask which equipped with a reflux condenser and (0.004 mol/0.35 g) of catalyst was added. The reaction mixture was heated to 130°C on oil bath for 8 h. the mixture was cooled the mixture at room temperature and washed with ethyl acetate (3 X 25 ml) and the solid catalyst was removed by filtration and transferred into separating funnel, 10 mL of NaHCO₃ was added to neutralize the product and washing by brine, the organic layer was evaporated and the product was dried with a sufficient amount of Na₂SO₄. The dried product was rotary-evaporated to remove the solvent.

3. Results and Discussion

Molar ratio of substrates effect: the minimum mole ratio of substrates used is a challenge to be met in economical requirements of any reaction. The molar ratio of oleic acid effect on the esterification reaction is illustrated in Fig. 1. The molar ratio of 1:1 (the oleic acid to the oleyl alcohol) yields 67% and decreased thereafter. The decreasing yield % of oleyl oleate ester at high oleyl alcohol concentration 1:2 and 1:3 may be due to the oleyl alcohol is a present at very high concentration and thus the viscosity of the liquid phase surrounding the catalyst molecule is increased leading to ineffective mixing of reactants. Further, the subsequent reduction in reaction rate (Gunawan and Suhendra, 2008). This result is similar to what was obtained by Abdul Rahman et al. (2001), where they found the best molar ratio to get oleyl oleate ester is 1:1 in presence of lipozyme as catalyst.

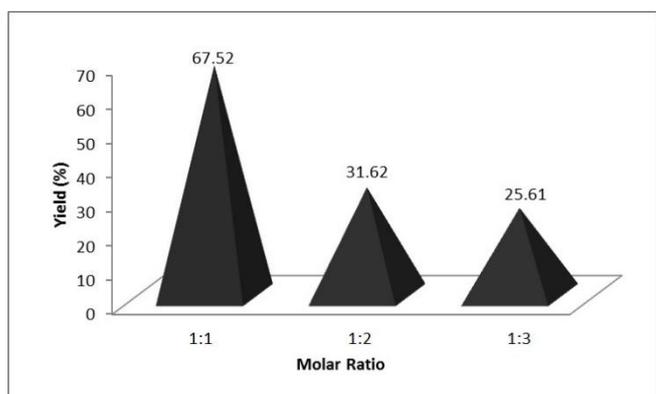


Fig. 1. Molar ratio effect on the esterification reaction of oleic acid and oleyl alcohol

Catalyst amount effect: the amount of catalyst used should be low as possible to obtain a good result. The oleyl oleate ester percentage yield produced at a constant value of catalyst NaHSO₄, and increased with increasing the amount of catalyst and reached maximum percentage yield of 83% at 10% catalyst of the weight of the oleic acid Fig. 2. According to Ramamurthy and McCurdy (1994), increased amount of catalyst will lead to an increase in the esterification rate (Ramamurthy and McCurdy, 1994). However, the percentage yield did not increase with increasing the amount of catalyst and sometimes it would decrease the yield of the product. This is also the same result, which was reported by Torres and Otero, where at saturation point, the catalyst have bonded all substrates (Torres and Otero, 2001).

Reaction temperature effect: temperature change of reaction can influence the activity and stability of the catalyst, substrate solubility and the reaction rate (Facioli and Barrera, 2001). The ester-

ification reaction of oleic acid with oleyl alcohol was done at six different reaction temperatures using NaHSO₄ as a catalyst Fig. 3. The percentage yield of oleyl oleate ester increased as temperature increase and the reaction temperature of 130 °C produced the highest yield 90% compared to other reaction temperatures.

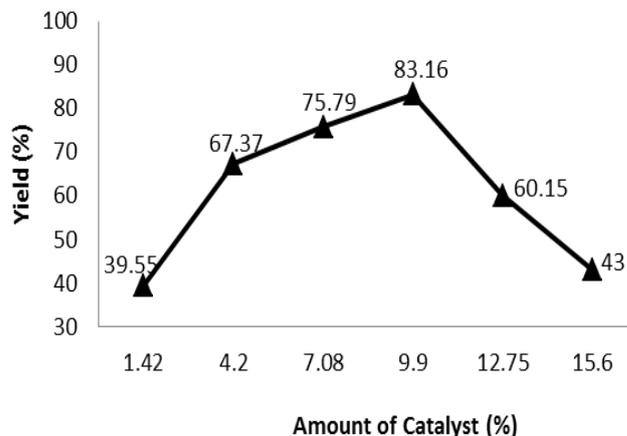


Fig. 2. Catalyst amount effect on the esterification reaction of oleic acid and oleyl alcohol

The solubility at low temperature is reduced with the subsequent high viscosity causing mass transfer limitations, retarding reaction rate and lowering final yields whereas, on increasing reaction temperature, substrate solubility improved in reducing mass transfer limitation and making the substrate more available to the catalyst (Facioli et al., 2001). Frequency collision of molecules was increased due to energy are received by high-temperature heat (Syamsul et al., 2010). While increasing the reaction temperature further decreased the percentage yield of oleyl oleate ester. Because water produced from reaction has two negative effects one to towards the catalyst where a fast interaction between the water and the catalyst might produce deactivation and thus reduce the rate of reaction; and the second one toward the reaction itself. Since this is an equilibrium reaction, the presence of water produced could shift the reaction towards the reactant, and therefore achieved a lower final percentage yield of oleyl oleate ester.

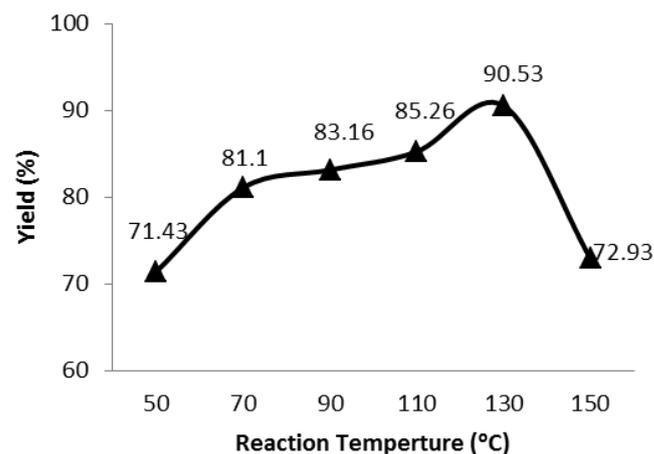


Fig. 3. Reaction temperature effect on the esterification reaction of oleic acid and oleyl alcohol

Reaction time effect: time is a good indication for catalyst performance and reaction progress. It can identify the shortest or the adequate time necessary to obtain yields and minimize process expenses (Yee et al., 1997). The reaction time can affect on the percentage yield thus good yields were obtained started with 40% within 2 h and 90% within 8 h reaction time after this time the yield will decrease within 10 h Fig. 4. The equilibrium state was achieved

thus the product concentration was unchanged and substrate concentration which leads to that the catalyst is saturated with a substrate (Manley et al., 2007).

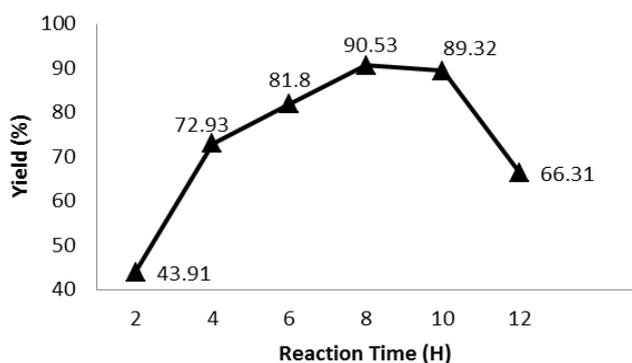


Fig. 4. Reaction time effect on the esterification reaction of oleic acid and oleyl alcohol.

The comparison between starting materials and product of the esterification reaction was achieved by using FTIR, ^1H and ^{13}C -NMR, Fig. 5 and Tables 1 and 2. FTIR spectrum shows C=O group at $1735\text{--}1750\text{ cm}^{-1}$, stretching vibration peak of =CH at $3000\text{--}3050\text{ cm}^{-1}$ while $3300\text{--}3400\text{ cm}^{-1}$ belong to OH group starting material (Silvestein and Webster, 1998). FTIR spectrum of wax ester show stretching vibration peak at 1739 cm^{-1} belongs to carbonyl stretching frequency of ester. However, the carboxylic acid bands which are OH group at 3338 cm^{-1} and carbonyl group at 1709 cm^{-1} were disappeared (Silvestein and Webster, 1998), Fig. 5.

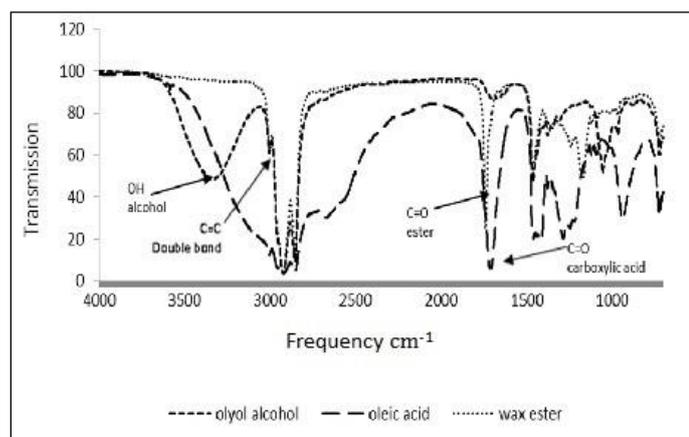


Fig. 5. The FTIR spectra of oleyl oleate, oleic acid and oleyl alcohol.

^1H -NMR and ^{13}C -NMR chemical shifts of the wax ester are compared with the literature values (Sharam et al., 2006). Notable the esterification evidence is the appearance of COOCH_2 peak at 4.02 ppm (Hwang and Erhan, 2005) and ^{13}C -NMR signals of the unsaturated bond (100–150 ppm), C-O bond (40–80 ppm) and carbonyl ester group (155–185 ppm) are performed, Table 2, (Awang et al., 2007).

Table 1

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

| Assignment | Chemical shifts, ppm | Chemical shift, ppm (Awang et al., 2007) |
|---------------------------------------|----------------------|--|
| $-\text{CH}_2\text{-COO}$ | 2.26 | 2.25 |
| $-\text{CH}=\text{CH}-$ | 5.32 | 5.43 |
| $\text{CH}_2\text{-O-CO}$ | 4.02 | 4.08 |
| CH_3 | 0.85 | 0.96 |
| CH_2 | 1.23–1.33 | 1.29–1.33 |
| $\text{C}=\text{C}-\text{C}-\text{H}$ | 1.85 | 1.96 |

Table 2

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

| Assignment | Chemical shifts, ppm | Chemical shift, ppm (Awang et al., 2007) |
|---------------------------|----------------------|--|
| C=O | 173.2 | 173.2 |
| C=C | 130.6 | 131.0 |
| C-O | 64.59 | 65.9 |
| CH_2 | 22.76–29.98 | 22.5–30.1 |
| $\text{CH}_2\text{-COO-}$ | 32.82 | 33.5 |
| CH_3 | 14.12 | 14.5 |

4. Conclusion

The heterogeneous catalyst (NaHSO_4) was used as catalyst and desiccant on the esterification synthesis of wax ester by using oleic acid with oleyl alcohol. The esterification was carried out and the ester produced was isolated in high yield at $130\text{ }^\circ\text{C}$ and 8 h. Thus, the synthesis of synthetic liquid wax esters has the potential of meeting the demand of these esters.

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