Lead (II) Nitrate Catalyzed Esterification Palmitic Acid with Alcohols

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Abstract: Esters has been long known in some applications that has been attempted to prepare in many fashion methods. Several catalysts used based on acid either solid or liquid has been known popular. A transition salt also has been intensively reported catalyzes esterification. Very few catalysts from Group A metal shown activities esterification catalysis. Lead (II) nitrate shown a good catalyst performance in esterification long chain fatty acid reacts with primary and secondary alcohol. Palmitic acid reacts with alcohols, glycerol, 1,2-propane diol as well as stearyl alcohol gives high yield ester respectively. All ester has been characterized in FT-IR, 1H NMR and 13C NMR spectrophotometer shown the yield was 90-97%.

1 INTRODUCTION

Oleochemical industry is still growing sustainable due to the product is needed in daily living. Esters for example have high demand as fuel, plasticizers, fragrance, adhesive and also as lubricants (Joseph, 2005; Mbaraka, 2006; Krause 2009; Martinez 2009). Catalysis esterification reactions can be performed in several manner catalyst such as, homogeneous acid include $AlCl_3$, HF, H2SO4. Although those catalysts bring high environmental risk and the cost inefficiency, this is still used in production industrial esters (Ziarani, 2013). Part of research to improve the environmental risk, then the heterogeneous catalyst has been developed. This catalyst system can be allowed to recovery, recycle and then reused (Gupta, 2007). Parallels to the chemical process environmentally, sulfonates acid functional was modified, by grafting with silica gel (Davison, 2008) anchoring to silica mesoporous (Keppelera, 2011), inorganic solid supported (Vijaykumar, 2012) that can be less toxic. Attempt to apply in chemical process esterification long chain acid, fatty acid with glycerol (alcohol multivalent), a sulfonate catalyst was used in a high condition (240 ^{0}C) (Sari, 2017).

In a relative new esterification catalyst development such as Barnstead acid salt, Sn (II) and Sn (IV) performs reaction long chain acid with alcohols to be esters. The key reaction is a forming bonding Sn-OR (Cardoso, 2009; da Silva, 2011; Ferreira, 2012). However the report is still limited on a simple alcohols. Due to Lead has a very similar chemistry to Tin, then it has been shown catalytic activity in esterification palmitic acid toward stearyl alcohol, diol and also triol as reported here.

2 MATERIALS AND METHODS

2.1 Materials

Materials used in this research $Pb(NO_3)_2$, 1,2-propane diol, 1, glycerol, octadecyl alcohol (stearyl alcohol), palmitic acid and m-xylene were purchased from Merck and used without pretreatment.

2.2 Analysis Method

^{1}H NMR and ^{13}C NMR spectra were recorded at 500 MHz on Agilent spectrometer. Wave number of carbonyl were recorded on spectrometer FT IR.

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2.3 Esterification Reaction

Into a round bottle flask provided a hotplate stirrer, a bar magnetic and a condensor, a mixture of xylene 30 ml; glycerol (1.84 g; 0.02 mol), palmitic acid (15.384 g; 0.06 mol) and lead (II) nitrate (0.02 g; $6x10^{-5}$ mol). The system was heated at 140 ^{0}C for 8 hours. The product mixture was distilled to free xylene, then extracted with n-hexane 2x 50 mL. The solution was washed with water 50 mL followed by addition with ethanol- water 30 mL. Finally the n-hexane fraction was dry with Na_2SO_4 anhydrous 5 g. After filtration, then the solution was evaporated and dried in vacuum, gave a solid was 14.526 g; 90% yield. Glyceryl tripalmitate was characterized with spectroscopy FT-IR and ^{1}H NMR ($CDCl_3$).

A similar work was done by change the alcohol, 1,2-propane diol (1.58 g ; 0.02 mol and stearyl alcohol (5.41 g; 0.02 mol) reacts toward palmitic acid (10.256 g; 0.04 mol) and (5.12g; 0.02 mol) respectively producing 1,2-propanyl dipalmitate (11.244 g; 95%) and stearyl palmitate (10.21 g; 97%).

3 RESULT AND DISCUSSION

3.1 Esterification Process

Reaction alcohols to palmitic acid catalyzed by lead (II) nitrate has been successfully to form esters. However the reaction took place in a consuming time. This is may be needed the evaluation catalyst amount to increase amount. Normally, the catalyst amount is proportional to speed of reaction. The end of the reaction shown that the catalyst turn to black powder more soluble in ethanol rather the product that allowable easy to separated from the ester product in the reaction. The black powder is a future challenge for investigated.

Based on the ratio product to catalyst, turn over frequency catalyst found 300- 323 per second.

3.2 Spectroscopy FT- IR

Product glyceryl tripalmitate shows wave number (ν C=Ocm-1) 1731, 1,2-propanyl dipalmitate 1739 and strearyl palmitate 1736. Figure 1 shows feature of FT IR spectrum of the esters.

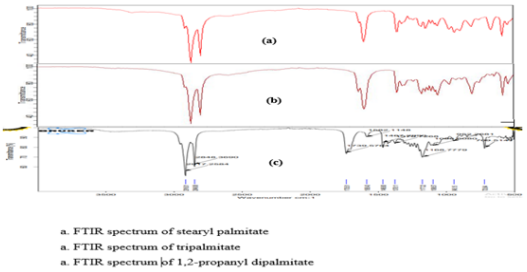


Figure 1: FT-IR Spectrum of the Esters.

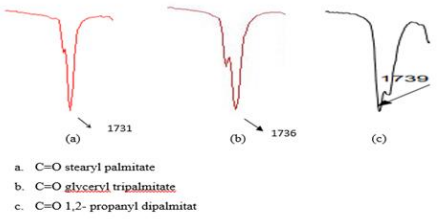


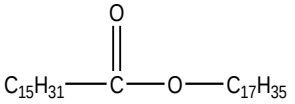
Figure 2: Carbonyl fashion on FT IR.

Spectrum FT IR shows on stearyl palmitate perform a single band C=O) at 1731 cm^{-1} with trace band at 1735 cm^{-1} (unknown) while in glyceryl tripalmitate shows two bands C=O, 1740 cm^{-1} (shoulder) and 1736 cm^{-1} (strong band) may be indicated two types of ester resulted 1 and 3 carbon atom which are equal contribution to IR spectra and the other one resulted from carbon atom 2 . The similar mode has also been indicated on 1,2-propanyl dipalmitate.

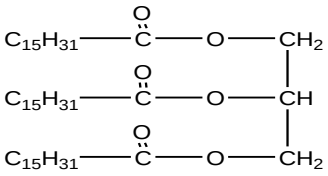
Analysis on ^{1}H NMR (500MHz, CDCl3) and ^{13}C NMR (125 MHz, $CDCl_3$). The data collected as below:

a) Stearyl palmitate: 1H NMR δ (ppm) 0.86 - 0.90 (br m, 6H), δ 1.26 - 1.30 (br s, 54H), δ 1.57-1.65 (br m, 4H), δ 2.29 (t, 2H), δ 4.05 (t, 2H)
   ^{13}C NMR(125 MHz, CDC_{13}) δ (ppm) 13.98, 22.13, 24.53, 25.54, 28.57, 28.73, 28.77, 28.93, 29.00, 29.05, 31.32, 32.57, 33.70, 60.76, 174.53.
b) Glyceryl tripalmitate: 1H NMR δ (ppm) 0.86 - 0.90 (br m, 2H), δ 1.26 - 1.30 (br s, 78H), δ 2.32 (t, 2H), δ 4.32 (t, 1H), δ 5.25 (t, 2H)
   ^{13}C NMR(125 MHz, CDCl3) δ 14.26, 22.85, 24.84, 29.22, 29.28, 29.40, 29.44, 29.52, 29.59, 29.64, 29.75, 29.76, 29.80, 29.81, 29.83, 29.84, 29.85, 32.08, 34.21, 34.36, 62.15, 68.93, 180.21.

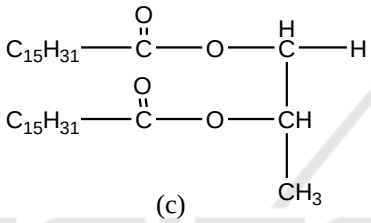
c) 1,2-propanyl dipalmitate: ^{1}H NMR δ(ppm) 0.86 - 0.90 (t, 3H), δ 1.19- 1.30 (br s, 27H), δ 1.57-1.65 (br m, 2H), δ 2.32-3.94 (t, 4H), δ 4.11 (t, 2H), δ 4.96 (m, 2H), δ 5.14 (m, 1H)



(a)



(b)



(c)

a. Structure of stearyl palmitate
b. Structure of glyceryl tripalmitate
c. Structure of 1,2-propanyl dipalmitate

Figure 3: Chemical Structure of a,b and c.

3.3 Yield of Reaction

Influence of Alcohols with palmitic acid catalyzed by $Pb(NO_3)_2$.

Stearyl palmitate (1-OH) 97%

Gyceryl tripalmitate (3-OH) 90%

1,2- propanyl dipalmitate (2-OH) 95%

The reaction alcohols in a same mole (0.02 mol) mono, diol and triol with palmitic acid at stoichiometric reaction gives a range of yield 97%, 95% and 90%. The alcohol might have steric effect on the reaction that shown in triol less yield of ester then the two others.

4 CONCLUSIONS

Lead (II) nitrate has a good catalyst esterification for long chain acid with long chain, multivalent alcohols. In future work, we need to show the catalyst performance a simple acid esterfied with a series alcohol chain.

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