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### Original Research Article

# Synthesis of polyol esters by *p*-toluenesulfonic acid catalyst as synthetic lubricant oils

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Polyol Esters

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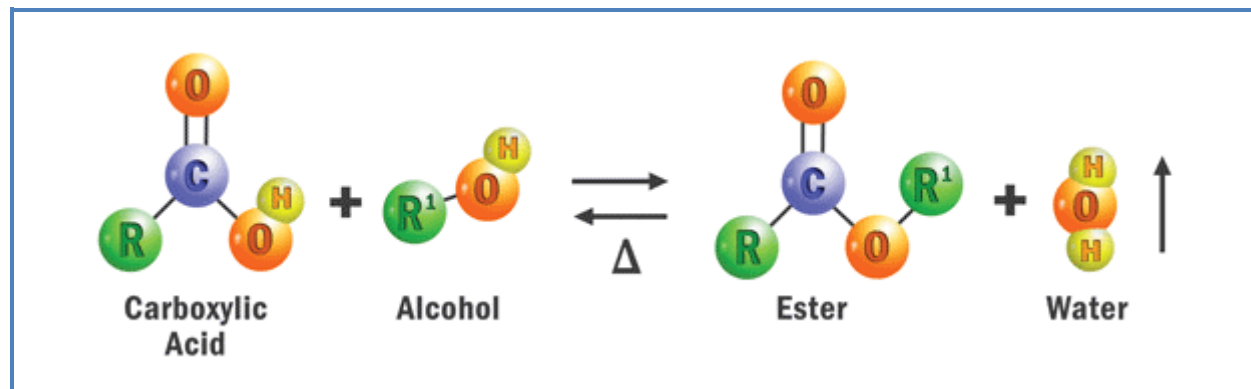
Trimethylolpropan ester

Synthetic oil

#### ABSTRACT

A most effective and less energy demanding method of producing fatty esters, polyol esters, by esterifying fatty acids, with a pentaerythritol and trimethylolpropan alcohols in the presence of an acid catalyst at elevated temperature wherein an azeotroping agent, particularly toluene, is used to facilitate continuous removal of water by distillation, formed as a by-product during the esterification reaction. The esterification reaction is completed within 5 hours, pentaerythritol and trimethylolpropan esters were produced.

### Graphical Abstract



## Introduction

Esterification and transesterification reactions usually carry out in hydrocarbon solvents, such as toluene. Homogeneous acid catalysts such as, sulfuric acid, methane sulfonic acid, and *p*-toluene sulfonic acid are the most conventional catalysts for this purpose. Application of these catalysts causes some difficulties such as corrosion, and environment problems [1, 2]. Therefore, development of new methods involving more efficient catalysts without needing for solvent has been noted. It is well known that the use of heterogeneous catalysts for liquid phase organic reactions can give a lot of benefits [3]. In such reactions, a clean reaction product solution is obtained after simple filtration, and the catalyst can be easily recovered. For this reason, some attention has been paid to the use of heterogeneous catalysts in esterification reactions [4, 5]. The use of heteropolyacids, silicoaluminophosphate molecular sieves [6], and sulfated zirconia [7] as heterogeneous catalysts for esterification and/or transesterification reactions has been reported earlier polyolester oil (POE oil) is a type of synthetic oil used in refrigeration compressors that is compatible with the refrigerants R-134a, R-410A and R-12 [8]. It is recommended by experts as a replacement for hydrofluorocarbons (HFCs). Along with R-134a mineral oil it is recommended as a replacement for R12 mineral oil [8] as R134a does not mix well with mineral oil. These wax-free oils are suggested for use with chlorine free HFC systems as they provide better lubrication and stability and are more miscible with HFC refrigerants. They can meet the lubricity requirements to those of mineral oils used with CFCs and HFCs. They are compatible with most lubricants in the market [9]. It is noted that the viscosity of the oil increases with temperature. The dispersion behavior of this oil has also been the subject of a lot of study. It is also considered by some to be a good additive to engine oil [10].

## Experimental

### Materials and methods

All materials were purchased from Merck Company. IR spectra were recorded with a Shimadzu FTIR-408 spectrophotometer as KBr pellets.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 400 AC spectrometer in  $\text{CDCl}_3$  as a solvent at room temperature.

### Typical procedure for preparation of polyol esters

A reaction mixture of pentaerythritol or trimethylolpropan and fatty acid, is transferred into a reaction flask. The reaction flask is equipped with a modified Dean-Stark distillation set-up, magnetic stirrer, condenser, dropping funnel and heating plate. Toluene (1 mol) is added to the

reaction mixture. *P*-toluenesulfonic acid is added to the reaction mixture when it has reached the temperature of 160 °C heating continued for not more than 5 hours. Water formed as by-product of the esterification reaction is removed continuously by means of distillation with the aid of toluene while toluene is recycled continuously back to the reaction mixture. After the reaction is completed, the crude product is cooled to ambient temperature. Then, excess solvent is removed from the crude product by means of rotary evaporation, *p*-toluene sulphonic acid catalyst is removed by repeated washing with water until the product produced is neutral. After that, the product is dried with anhydrous sodium sulphate and the hydrated sodium sulphate is later-removed from the dried product. The dried product is further purified by using a column packed with silica gel. Trace solvent is further removed by a vacuum pump and finally unreacted fatty acid is removed by means of vacuum distillation. Unreacted fatty acid would remain as residue while pentaerythritol and trimethylolpropan ester would be collected as distillate (87-91%). Reaction pathways were shown in Scheme 1, 2 and 3.

#### *Pentaerythritoltetrahexanoate ester*

This ester was prepared according to the general procedure by using pentaerythritol (1.2 mol) and hexanoic acid (5 mol), yield 87%, IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 2970, 2910, 2845, 1740, 1455, 1380, 1245, and 1110.  $^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.12 (s, 8H), 2.31 (t, 8H,  $J = 7.5$  Hz), 2.05-1.95 (m, 8H), 1.33-1.25 (m, 16H), 0.89 (t, 12H,  $J = 6.9$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  173.5, 62.7, 43.8, 34.1, 31.2, 24.6, 22.2, 13.8.

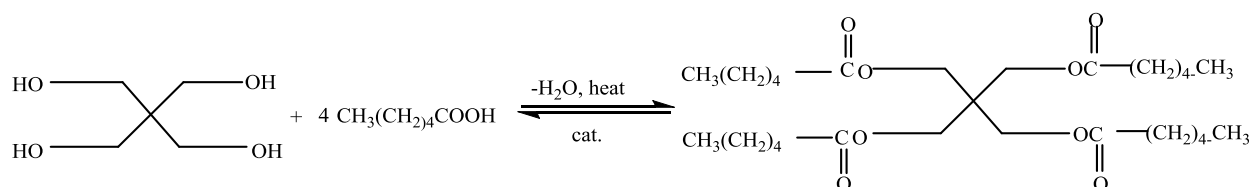
#### *Trimethylolpropantrihxanoate ester*

This ester was prepared according to the general procedure by using Trimethylolpropan (1.2 mol) and hexanoic acid (4 mol), yield 89%, IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 2970, 2930, 2865, 1740, 1465, 1250, and 1100.  $^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.98 (s, 6H), 2.27 (t, 6H,  $J = 7.6$  Hz), 1.54 (quin, 6H,  $J = 7.4$ Hz), 1.44 (q, 2H,  $J = 7.6$ ), 1.26 (m, 12H), 0.86 (t, 3H,  $J = 7.2$ ), 0.85 (t, 9H,  $J = 7.6$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  172.3, 62.5, 39.5, 33.0, 30.1, 23.5, 21.9, 21.1, 12.78.

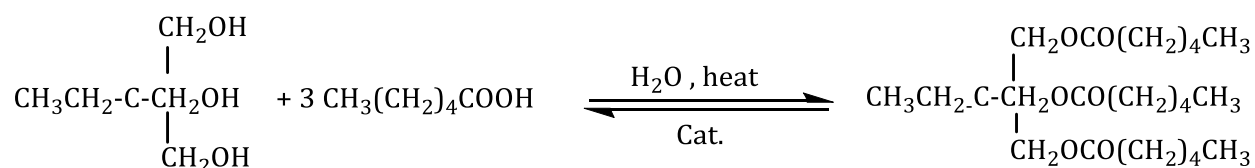
#### *Trimethylolpropantrioctanoate ester*

This ester was prepared according to the general procedure by using Trimethylolpropan (1.2 mol) and hexanoic acid (4 mol), yield 90%, IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 2940, 2880, 1740, 1470, 1395, 1250, and 1100.  $^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.95 (s, 6H), 2.23 (t, 6H,  $J = 7.47$ Hz), 1.54 (quin, 6H,  $J$

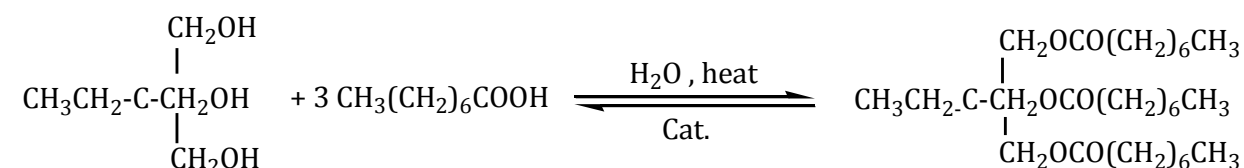
= 7.21 Hz), 1.41 (q, 2H,  $J = 7.6$ Hz), 1.25-1.15 (m, 24H), 0.82 (t, 3H,  $J = 7.4$ Hz), 0.81 (t, 9H,  $J = 7.05$  Hz).  
 $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  21.4, 21.8, 23.7, 23.8, 27.4, 27.9, 30.4, 33.0, 33.1, 39.4, 62.4, 172.2.



**Scheme 1.** Synthesis of pentaerythritol tetrahexanoate ester



**Scheme 2.** Synthesis of trimethylolpropanetrihexanoate ester



**Scheme 3.** Synthesis of trimethylolpropanetrioctanoate ester

## Results and discussion

A process of producing fatty ester comprising the steps of **I**) direct esterifying fatty acid with a neopentylpolyol alcohol in the presence of an acid catalyst at a temperature in the vicinity of 110 °C-150 °C. **II**) Using toluene to facilitate continuous removal by distillation, of water formed as a by-product during the esterification reaction. **III**) Purifying the product obtained from step **(II)** by removing acid catalysts and impurities.

The esterification reaction can be conducted at a relatively moderate temperature and yet achieve and on version rates over short reaction time by using toluene, in order to an azeotroping agent to assist the removal of water formed as a by-product of the reaction, thus drive the reaction to completion. Polyolesters are formed from polyols with a quaternary carbon atom (neopentyl alcohols) as for example pentaerythritol, trimethylolpropan. The reaction conditions and yields of different esters are summarized in Table 1.

In this study, the synthesis of polyol esters by fatty acids in the presence of *p*-toluene sulphonic

acid catalyst has been investigated. Thus, in order to get polyol esters with good quality, we tried to facilitate the production technology by finding a desirable method and accompanied avoiding the waste of energy and materials, as a result, the overall price which can be reduced has no bioenvironmental pollution.

**Table 1.** The reaction conditions and yields of different esters are summarized

Product	Temperature (°C)	Time reaction (h)	Catalyst (mass%) <sup>a</sup>	Yield (%)
<b>1a</b>	120	5	3.2	87
<b>1b</b>	125	5	2.6	89
<b>1c</b>	110	5	2.6	90

## Conclusion

Lubricants based on polyol esters are economical and have seen considerable development as synthetic lubricants in automotive applications, marine diesel engines, transmission systems, and the aerospace industry. The fatty esters synthesized also renowned for their film strength and increased lubricity which is useful in reducing energy consumption in many application.

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