



## Screening of solid base catalysts on palm oil based biolubricant synthesis



Choon Tah Ivan-Tan <sup>a, b</sup>, Aminul Islam <sup>a, c, d, \*</sup>, Robiah Yunus <sup>e</sup>, Yun Hin Taufiq-Yap <sup>a, b, \*\*</sup>

<sup>a</sup> Catalysis and Science Research Center, Faculty of Science, University Putra Malaysia, 43400, UPM Serdang, Selangor, Malaysia

<sup>b</sup> Department of Chemistry, Faculty of Science, University Putra Malaysia, 43400, UPM Serdang, Selangor, Malaysia

<sup>c</sup> Faculty of Engineering, Universiti Malaysia Sabah, 88400, Kota Kinabalu, Sabah, Malaysia

<sup>d</sup> Energy Research Unit, University Malaysia Sabah, 88400, Kota Kinabalu, Sabah, Malaysia

<sup>e</sup> Institute of Advance Technology, Universiti Putra Malaysia, 43400, UPM Serdang, Selangor, Malaysia

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### ABSTRACT

The activity of solid base catalysts with selected dopants on the synthesis of trimethylolpropane triesters (TMPTE) biolubricant from palm oil methyl esters (POME) was performed in this study. The morphological and structural studies of synthesized catalysts were carried out using field emission scanning electron microscopy, X-ray diffraction (XRD), temperature programmed desorption (TPD-CO<sub>2</sub>), fourier transform infrared spectroscopy (FTIR), energy dispersive analysis by X-ray (EDX) and Brunauer–Emmett–Teller (BET) and gas chromatography (GC). The effects of temperature, time and the catalyst amount on the catalytic performance of different solid base catalyst with selected dopants were appraised. Under the optimized reaction conditions of 1 %w/w mixed oxides of Ca and Sr catalyst with 5 %w/w SrO on CaO, at 180 °C, 2 mbar vacuum pressure and 240 min of reaction time, TMPTE was successfully synthesized with 88% of yields. The type of metal oxide and mixed metal oxides demonstrated a significant effect on the physical property of the catalyst and its catalytic activity.

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### 1. Introduction

The existence of more sophisticated engines and machineries leads to a demand for more efficient and higher-performance lubricants. Synthetic lubricants are one of the solutions for such demand due to how easily they can be chemically modified to meet certain specification required by the engines and machineries. There is a growing interest on development of vegetable oil-based lubricant or commonly also known as biolubricant. Biolubricants have lesser threat to the environment and has shown to have better lubricity characteristics as compared to mineral oil-based lubricant (Salimon et al., 2011). On the contrary, mineral oil-based lubricants are harmful to the environment due to its toxicity and are not readily bio-degradable (Bartz, 1998).

Vegetable oil-based lubricants have their own limitations

despite being more desirable over mineral oil-based lubricants, e.g., oxidative, thermal, and hydrolytic stability, and inadequate low temperature fluidity due to high pour points (Wilson, 1998). The limitations mentioned above can be reduced by chemically modifying the structures of the vegetable oils, such as through transesterification of vegetable oil methyl esters and branched neopolyols like trimethylolpropane (TMP) to produce polyol esters (Uosukainen et al., 1998). Polyol esters molecules derived from this type of multi-functional synthetic alcohol are chemically more stable because of their quaternary or neopentyl carbon (Akerman et al., 2011). Trimethylolpropane Triesters (TMPTE) is one kind of polyol esters which is classified under Group V base oil and has been used as base fluids in lubricants (Nagendramma and Kaul, 2012). Depending on the properties of lubricant needed for certain applications such as hydraulic oil or metalworking fluid, the polyol esters can be blended with other base oil and additives to meet the specifications required (Chang et al., 2015). This method of modification has proved to be useful in reducing the mentioned limitations above especially in the area of improvement of the oxidative and thermal stability. The improvement in oxidative and thermal stability is made possible because of hydrogen atom on the β-carbon position of palm oil is eliminated (Huang et al., 2004). The

\* Corresponding author. Faculty of Engineering, Universiti Malaysia Sabah, 88400, Kota Kinabalu, Sabah, Malaysia.

\*\* Corresponding author. Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, 43400, UPM Serdang, Selangor, Malaysia.

E-mail addresses: [aminul03211@yahoo.com](mailto:aminul03211@yahoo.com) (A. Islam), [taufiq@upm.edu.my](mailto:taufiq@upm.edu.my) (Y.H. Taufiq-Yap).

transesterification reaction includes three consecutive reactions in the presence of a catalyst. Monoesters (ME) and diesters (DE) of TMP are formed as intermediate products towards the final stage of the reaction producing TMP triesters (TMPTE). The overall reaction stoichiometry requires 1 mol of TMP and 3 mol of methyl esters, resulting in an overall reaction as Eq. (1).



In order to obtain high yield of TMPTE, the presence of catalyst in the transesterification reaction medium plays an important role in increasing the yield. There have been reports of different types of catalysts such as homogeneous or heterogeneous ones with basic or acidic nature, or enzymes were used for the transesterification reaction. Taking an example from research where alkaline homogeneous catalyst such as sodium methoxide was used for the reaction (Naidir et al., 2012). Although high yield of TMPTE was obtained, the catalyst is highly corrosive in nature and tends to react with free fatty acids in the process, producing unwanted soap at the end of the reaction (Serio et al., 2005).

Another example where acidic homogeneous catalyst such as sulphuric acid being used for the esterification reaction to produce trimethylolpropane esters. In this experiment, 98.6% of trimethylolpropane triester was synthesized (Arbain and Salimon, 2010). Despite the ability of both basic and acidic homogeneous catalyst to help in the reaction to produce trimethylolpropane triester with yield as high as 98.6%, these types of catalysts also have their limitations, especially in posing serious threat to the environment due to their corrosive nature. It is also challenging in catalyst-product separation process where multiple washing of the catalysts are needed due to their homogeneity with the product (Sreeprasanth et al., 2006). There are also studies producing trimethylolpropane esters by enzyme as biocatalyst, for instance lipase such as candida rugosa biocatalyst was able to give reasonably high yield of TMPTE at 70% of triester with low reaction temperature at 47 °C. However, a long reaction time of up to 72 h was required to achieve the result (Uosukainen et al., 1998). Apart from the long reaction time, there were also reports on biocatalysts regarding their operational ability in a reaction which were greatly affected by free fatty acids and methanol (Luan et al., 2015). Due to the problems mentioned for homogeneous acidic and basic catalysts and biocatalysts, the development of heterogeneous catalysts have gained much attention lately in order to overcome or find solution for the problems faced. The reason is that heterogeneous catalysts is non-toxic in nature due to the ability of them being separated from the product easily and can be reuse in some cases. Previous studies incorporated calcium methoxide as heterogeneous base catalyst for the transesterification reaction between methyl esters and TMP. Though high yield was obtained, long reaction time up to 8 h was required (Chang et al., 2012). Thus, the aim of this work is to improve the yield of trimethylolpropane triesters (TMPTE) by screening of solid base catalysts. Catalyst characterizations and the effects of the operating variables on the yield of TMPTE were appraised.

## 2. Materials and methods

### 2.1. Chemicals

Palm Oil Methyl Ester was obtained from Carotino Sdn. Bhd (Malaysia). Trimethylolpropane, 2-ethyl-2-hydroxymethyl-1,3-propanediol (TMP) (assay >98%) purum grade were purchased from Sigma Aldrich Sdn. Bhd. (Malaysia), calcium oxide (CaO) was purchased from Fischer Scientific UK Ltd. and strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ ) was purchased from Chemie AG (Buchs, Switzerland).

For gas chromatography, ethyl acetate (GC grade) and n-hexane (HPLC grade) were acquired from Fisher Scientific Sdn. Bhd. (Malaysia), while N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (98%) was purchase from Acros Organic, Belgium.

### 2.2. Synthesis of CaO and SrO mixed oxides catalysts

Mixed oxides of CaO and SrO were prepared by wet impregnation method where the precursor, CaO was first suspended in deionised water of 50 mL in volume with continuous stirring using a magnetic stirrer. Then  $\text{Sr}(\text{NO}_3)_2$  was dissolved in another beaker in 10 mL of deionised water depending on the desired amount (5, 10, 15 and 20 %w/w) of SrO on CaO. After strontium nitrate has been fully dissolved, it was added drop-wise into the beaker containing  $\text{Ca}(\text{OH})_2$ . The mixture was left to stir for 6 h for complete and homogeneous impregnation of strontium ion into  $\text{Ca}(\text{OH})_2$  and subsequently dried in oven for 24 h to remove the excess water. After the drying process, the powder was grounded and calcined at 900 °C for 8 h to completely remove the water moisture trapped within the powder and also to obtain the oxides of the mixed metal by getting rid of their anhydrous form.

### 2.3. Synthesis of trimethylolpropane triesters

Experiment was carried out using batch reactor where the setup includes a hot plate stirrer, silicone oil bath, a 250 mL round bottom three-necked flask made of borosilicate glass, a PTFE coated magnetic stirrer bar, a reflux condenser, a mercury thermometer, and a sampling port. The reflux condenser was connected to a vacuum line which was equipped with a relief valve, accumulator and a vacuum trap. At the end of the vacuum line was a rotary vane vacuum pump which provide various vacuum conditions required during the reaction, and the vacuum level was controlled by an relieve valve mentioned earlier. POME was dried in oven at temperature of around 110 °C for 24 h before the reaction to ensure it is free from trapped moisture. After setup completion of the reactor, a known amount of TMP was added to the reactor and was melted through heating at 60 °C with continuous stirring under vacuum condition. The temperature was maintained at 60 °C for about 15 min to remove moisture from the hygroscopic TMP. A calculated amount of POME according to the respective molar ratio of TMP:POME was then introduced into the reactor and the reaction mixture was heated to the reaction temperature. Having reached the desired temperature, a desired amount of catalyst was added into the reactor. The reaction was then carried out under the required vacuum condition until the desired reaction of time. The product, in a solid form consisting of catalyst and traces of soap was then separated from the liquid portion of the product by centrifuging (tabletop centrifuge: model-4000) at 4000 rpm for 10 min when the reaction was completed.

### 2.4. Catalysts characterization

X-ray diffraction (XRD) measurement was carried out on Shimadzu Model XRD-6000 with its diffractometer which employs Cu-K $\alpha$  radiation generated by a Philips glass diffraction X-ray tube broad focus 2.7 kW type to produce diffraction patterns from powder crystalline samples at ambient temperature. All the catalysts were analyzed in the range of 10° to 70° 2 $\theta$  at the scanning speed of 1° ute $^{-1}$ .

Total surface area of the catalysts were characterized by Brunauer-Emmer-Teller (BET) method which was carried out by nitrogen adsorption at the temperature of 77 K and was conducted by using Thermo Finnigan Sorptomatic 1990 series nitrogen adsorption/desorption analyzer.

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