UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERISATION OF CaO-xSrO CATALYST FOR PRODUCTION OF PALM-BASED TRIMETHYLOLPROPANE TRIESTERS

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By

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SYNTHESIS AND CHARACTERISATION OF CaO-xSrO CATALYST FOR PRODUCTION OF PALM-BASED TRIMETHYLOLPROPANE TRIESTERS

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Chairman **: Professor Taufiq-Yap Yun Hin, PhD**
Faculty **: Science**

Presently, interest on development of plant-based lubricant or biolubricant is increasing. This is due to its biodegradable property, renewable and non-toxicity when compared to mineral oil-based lubricant. The focus of this study was to synthesise calcium oxide mixed with strontium oxide (CaO•xSrO) where x is different composition of strontium oxide calculated based on the weight of calcium oxide as heterogeneous mixed metal oxides base catalysts. The catalyst (CaO•xSrO) was synthesised using wet impregnation technique. The synthesised catalysts were then characterised by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), scanning electron microscopy with energy dispersive X-ray microscopy (SEM/EDX) and temperature-programmed desorption of carbon dioxide (TPD-CO_2). From the characterisations, catalysts synthesised (CaO•xSrO) shown to have high basic strength when SrO was impregnated on CaO besides providing alternate basic site to the synthesised catalyst (CaO•xSrO). The XRD and SEM-EDX data also showed that SrO on CaO was successfully synthesised with the detection of composition of SrO element using both XRD and SEM-EDX instrument. The synthesised CaO•xSrO catalysts were used to synthesis trimethylolpropane triesters (TMPTE) by transesterification of trimethylolpropane (TMP) and palm oil methyl esters (POME) to yield the product of TMPTE. TMPTE was deemed as a potential biolubricant basestock due to its excellent lubricity, viscosity–temperature characteristics, and low volatility. The synthesised product of TMPTE was analysed by gas chromatography - flame ionization detector (GC-FID) and fourier transform infrared (FTIR) for compositional study and functional group study respectively. The optimum conditions were obtained with 240 minutes reaction time using CaO•5SrO as catalyst, reaction temperature of 180 ºC, 1 %w/w catalyst loading to weight of POME and TMP, 6:1 of POME/TMP molar ratio at a fixed vacuum pressure of 2.5 mbar. The yield of final product (TMPTE) was found out to be 88.5% using the optimum conditions stated.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

SINTESIS DAN PENCIRIAN PEMANGKIN CaO-xSrO BAGI PENGELUARAN TRIMETILPROPANA TRIESTERS YANG BERASAKAN DARY MINYAK SAWIT

Oleh

IVAN TAN CHOON TAH

JUN 2017

Pengerusi : **Profesor Taufiq-Yap Yun Hin, PhD**
Fakulti : **Sains**

Pada masa kini, minat ke atas perkembangan pelincir yang berasaskan tumbuhan atau lebih sering digelar sebagai biopelincir semakin meningkat. Ini adalah kerana biopelincir adalah biodegradasi, boleh diperbaharui dan tidak toksik berbanding dengan pelincir yang berasaskan minyak mineral. Fokus kajian ini adalah mensintesis campuran kalsium oksida dengan strontium oksida (CaO•xSrO) sebagai pemangkin bes campuran oksida logam heterogen, dimana x adalah komposisi strontium oksida yang berlainan yang dikira berasaskan berat kalsium oksida. Pemangkin (CaO•xSrO) disintesis dengan impregnasi basah. Pemangkin-pemangkin CaO•xSrO yang disintesis telah dikajikan dengan menggunakan belauan sinar-X (XRD), pancaran medan mikroskopi elektron penskanan (FE-SEM), mikroskopi elektron penskanan dengan sebaran tenaga sinar-X (SEM/EDX) dan penyahjerapan suhu terancang-karbon dioksida (TPD-CO_2). Dari data pencirian yang dibuat, pemangkin yang disintesis (CaO•xSrO) menunjukan mereka mempunyai kekuatan bes yang tinggi apabila SrO diimpregnasikan ke atas CaO, selain itu, SrO juga bantu dalam menyediakan tapak bes alternatif pada pemangkin yang disintesis (CaO•xSrO). Data XRD dan SEM-EDX juga menunjukkan bahawa SrO berjaya diimpregnasikan ke atas CaO dengan komposisi SrO boleh dikesan dengan kedua-dua alat tersebut. Pemangkin-pemangkin CaO•xSrO yang telah disintesiskan kemudiannya digunakan untuk mensintesiskan trimetilolpropana triesters (TMPTE) dengan transesterifikasi trimetilolpropana (TMP) dengan metil ester minyak sawit (POME) bagi menghasilkan produk TMPTE. TMPTE adalah dianggapkan mempunyai potensi untuk dijadikan sebagai stok asas bagi minyak biopelincir, ini disebabkan oleh ianya mempunyai sifat linciran yang cemerlang, ciri-ciri kelikatan-suhu yang sangat baik, dan ruapan yang rendah. Produk TMPTE yang telah disintesiskan kemudiannya dianalisis oleh kromatografi gas - pengesan nyala pengionan (GC-FID) dan transformasi fourier inframerah (FTIR), masing-masing untuk kajian komposisi dan kumpulan berfungsi. Keadaan optimum telah dicapai dengan menggunakan pemangkin CaO•5SrO, suhu tindak balas 180℃, muatan 1 %w/w pemangkin kepada berat POME dan TMP, nisbah molar POME/TMP 6:1, tekanan vakum ditetapkan pada 2 mbar dan masa tindak-balas

selama 240 minit. Sebanyak 88.5% hasil produk akhir TMPTE telah dicapai dengan menggunakan keadaan optimum yang dinyatakan.

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I certify that a Thesis Examination Committee has met on 1 June 2017 to conduct the final examination of Ivan Tan Choon Tah on his thesis entitled "Synthesis and Characterisation of CaO-xSrO Catalyst for Production of Palm-Based Trimethylolpropane Triesters" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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This is to confirm that:

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Name of Member of Supervisory Committee:	Professor Dr. Mohd. Zobir Hussein

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller Surface Area Measurement
Ca	Calcium
CaO	Calcium Oxide
CaO•10SrO	10 %w/w of Strontium mixed Calcium Oxides
CaO•15SrO	15 %w/w of Strontium mixed Calcium Oxides
CaO•20SrO	20 %w/w of Strontium mixed Calcium Oxides
CaO•5SrO	5 %w/w of Strontium mixed Calcium Oxides
CaO•xSrO	Strontium Oxide Mixed Calcium Oxide (where x=5, 10, 15, 20 %w/w Strontium Oxide on Calcium Oxide)
$NaOCH_3$	Sodium Methoxide
DE	Diesters
FE-SEM	Field Emission - Scanning Electron Microscopy
FT-IR	Fourier Transform - Infrared Spectroscopy
GC	Gas Chromatography
GC-FID	Gas Chromatography by Flame Ionization Detector
HOVO	High Oleic Vegetable Oils
ME	Monoesters
MgO	Magnesium Oxide
PAG	Polyalkylene Glycols
PAO	Polyalphaolefins
PE	Polyol Esters
POME	Palm Oil Methyl Esters
SEM/EDX	Scanning Electron Spectroscopy with Energy Dispersive X-ray
Sr	Strontium

SrO	Strontium Oxide
$Sr(OH)_2$	Strontium Hydroxide
TE	Triesters
TMP	Trimethylolpropane
TMPE	Trimethylolpropane Esters
TMPTE	Trimethylolpropane Triesters
TPD-CO_2	Temperature Programmed Desorption by Carbon Dioxide
VI	Viscosity Index
XRD	X-ray Diffraction Analysis
ZnO	Zinc Oxide

CHAPTER 1

INTRODUCTION

1.1 Background of Study

1.1.1 Lubricants

Lubricant plays an important role in reducing friction between two surfaces by providing a thin layer of protection film which prevents two surfaces to be in direct contact that may lead to surface wear, thus causing loss of energy transfer and reducing the efficiency of the overall mechanic function. Besides, lubricant can also lower machine's operating temperature by reducing friction of two surfaces as mentioned earlier, and it can also help to increase the sealing in machine parts with the formation of thin film on the surface.

The history of the modern day synthetic lubricant can be tracked way back to year 1877 where chemists Charles Friedel and James Mason Crafts successfully synthesised hydrocarbon-based lubricating oils. However in 1929, Standard Oil Company of Indiana tried to commercialize synthetic hydrocarbon but was unsuccessful due to the lack of demand for such oil at that time. Nevertheless, the interest in synthetic lubricants were revitalised during World War II where there was shortage of mineral-oil based feedstock for lubricant. Furthermore, gelation of mineral oil-based lubricant actually occurred during that time under certain conditions like low temperature environment which eventually caused decrease in efficiency in lubricating the military machinery that leads to overheating or machinery parts ceased to move.

The interest towards synthetic lubricants did not stop with the ending of World War II. In 1937, ester-based lubricants have emerged to be of interest by researchers during the Zurich Aviation Congress. Fast forward to the current date, the demand for newer, more efficient and higher performance lubricants is increasing due to the sophistication of modern days engines and machineries. Thus, in order to meet those demands, modifications have to be made to the mineral-oil based lubricant or alternative raw materials need to be found. These demands lead synthetic lubricants to be on the focus as they are easy to be chemically modified to meet certain specifications that were required by modern days engines and machineries (Sharma *et al.*, 2006; Salimon *et al.*, 2011).

Furthermore, besides the required properties that were available from synthetic lubricants, another reason to look for alternatives in lubricant was also due to the increasing demand. Taking Southeast Asia alone for example, , it can be seen that from Figure 1.1, there will be an increasing demand for lubricant in the region with Compound Annual Growth Rate, CAGR of up to 4.7% from year 2014 to year 2019. This trend shows a good indication of alternative of mineral oil-based lubricant to be researched and produced in order to cope with the increasing demand.

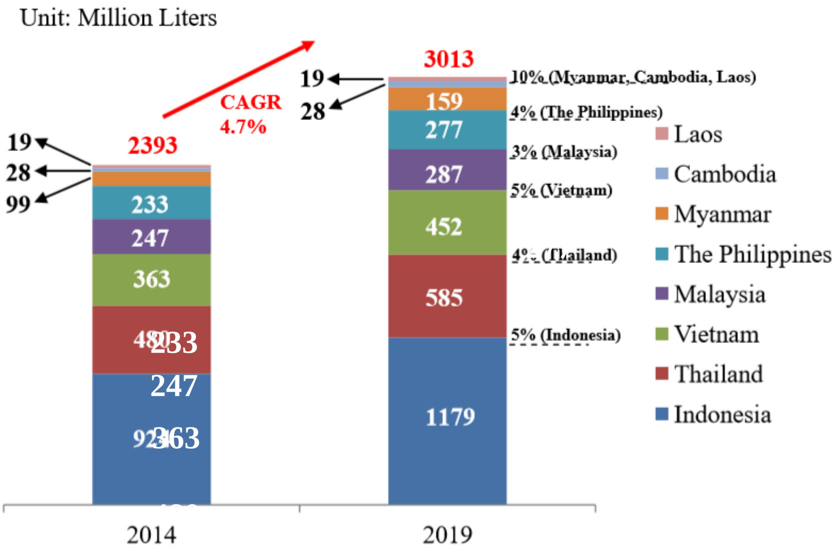

Figure 1.1 : Estimated Growth of Lubricant Demand in Southeast Asia
(Source: Ipsos Business Consulting Analysis)

One of the raw materials in synthetic lubricants is esters-based. They have been proven to be very useful and full of benefits. For example, esters-based lubricants are environmental friendly due to the ease of them to bio-degrade and are also renewable as they can be synthesised from vegetable oil (Bartz, 1998). Vegetable oil-based esters lubricants, which sometimes are also referred as biolubricants also give desirable characteristics. For instance, they possess good extreme-temperature performance where they can maintain their viscosity but yet at the same time protects the machinery parts at elevated temperature operations. The emergence of biolubricant was not only caused by their interesting characteristics; it is also due to the boom of petroleum prices around 1970s which then leads to the desperate need to find alternatives raw materials to mineral-based lubricant.

1.1.2 Biolubricants

Biolubricant or also known as vegetable oil-based lubricant is generally categorised as synthetic lubricant. Besides vegetable oils, synthetic lubricants may include modified chemicals like polyalphaolefins, synthetic esters and polyalkylene glycols (Lathi *et al.*, 2007; Pirro and Wessol, 2001). As compared to mineral oil-based lubricants, these synthetic lubricants can be synthesised to have comparable mineral-oil based lubricant characteristics. Furthermore, with proper additives packages added, they can even perform better than mineral-oil based lubricants in terms of reliability and specifications. In this project, the biolubricant produced was esters-based lubricant derived from palm oil. It was done by modifying the palm oil molecule's structure to form new natural synthetic esters which is more environmental friendly and renewable (Yunus *et al.*, 2003).

The esters synthesised by transesterification will result in long chain polyol esters where were proven to be useful as lubricant in steel-rolling industry, as hydraulic fluids and outdoor lubricants (Remmelmann and Murrenhoff, 1998). Polyol esters in this project will be derived from trimethylolpropane (TMP). The transesterification was done by reacting methyl esters of palm oil with TMP [2-ethyl-2-(hydroxymethyl)-1, 3-propanediol] using mixed-oxides of group II alkaline metal as catalyst. Figure 1.2 shows the molecular structure of palm oil methyl ester and palm-based TMP esters and Figure 1.3 shows the route of the transesterification reaction.

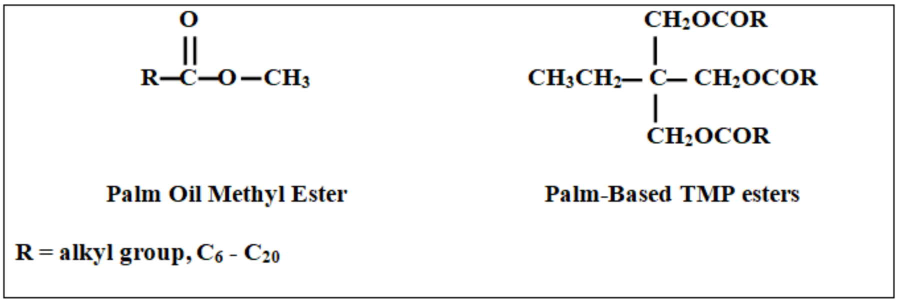

Figure 1.2 : Molecular Structures of Palm Oil and Palm-Based Trimethylolpropane Esters

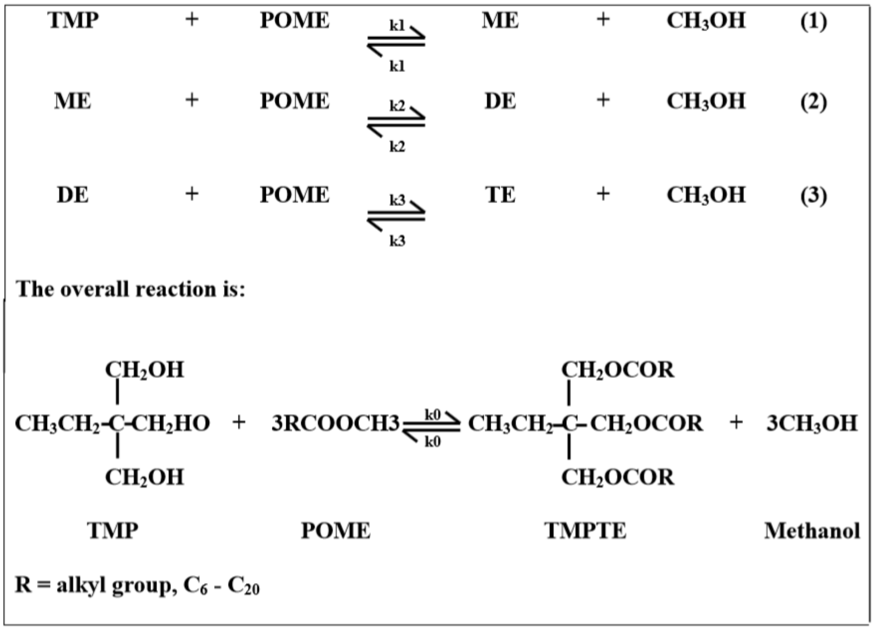

Figure 1.3 : Reaction for Transesterification of POME and TMP

1.1.3 Transesterification of Esters

Transesterification was done in the presence of alkaline catalysts as mentioned . This type of reaction offers advantages where it improves the oxidative and thermal stability of the synthesised TMP ester, in which this is a property rarely found in vegetable oils. The characteristics are made possible because the synthesised trimethylolpropane triesters (TMPTE) is without hydrogen molecule on the β-carbon position (Gunstone, 1986). Figure 1.4 shows esters with hydrogen molecule on the β-carbon position which contribute to the lower oxidative and thermal stability of the esters compound reacted. From the figure, only radical decomposition can occur for ester without β-Hydrogen, which requires more energy, thus higher temperature is needed for the decomposition to occur (Eychenne *et al.*, 1998).

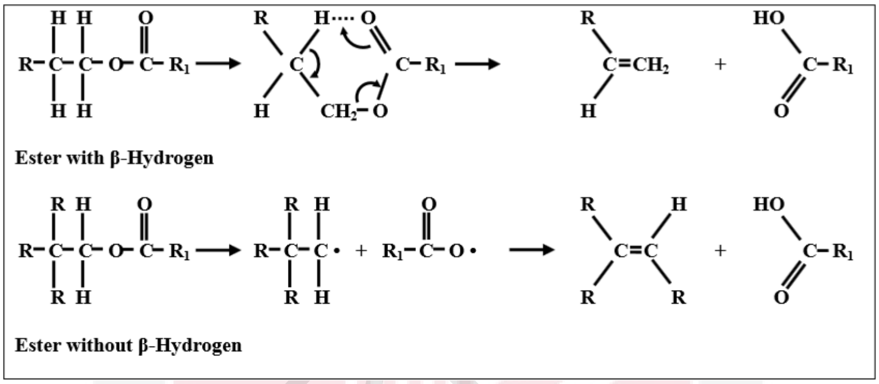

Figure 1.4 : Thermal Destruction of Esters with β-Hydrogen

1.1.4 Catalyst

Catalysts by definition are substances that were added into a reaction which can increase the rate of the reaction. In addition, catalyst can also increase the selectivity of a reaction by allowing only certain molecules to react on their surface. By doing so, they can even reduce dangerous by-product of some reaction by eliminating the possibility of that reaction to occur. In depth, catalysts work by providing an alternative path of the reaction with lower reaction energy thus increasing the overall rate of the reaction as the energy required are now can be easily achieved.

Catalysts can exist in two different state in a reaction. Namely, as homogeneous or heterogeneous catalyst. For catalysts that are in homogeneous state with the reaction, they appear to be in the same phase as the reactants. In other words, when the reactants are liquid, then the phase of the catalyst will also be in liquid form. Vice versa for heterogeneous catalysts, they exist in different phase to that of reactants.

Generally, heterogeneous catalysts are in solid form in most reaction whereas the reactants are in liquid state. These catalysts are also known as surface catalysts because the reaction starts from their surface.

1.2 Problem Statement and Scope of Study

Production of biolubricant are normally done using homogeneous catalysts due to the ability of these catalysts to provide high yield of the final product. A research done by Yunus *et al*. (2002) for transesterification of TMP and palm oil mill effluent (POME) to produce triesters of TMP (or also known as trimethylolpropane triesters, TMPTE), the homogeneous alkaline catalyst of sodium methoxide, $NaOCH_3$ was able to obtain high yield of approximately 98 wt% TMPTE. However, the separation process for the catalyst appeared to be rather cumbersome because the catalyst would appear to be in the same phase as the reaction materials thus suitable solvent was needed to separated the catalyst with product. This step has high chance of having loss of product. Besides, if the catalyst is not properly separate from the final product, it would cause the product to have corrosive nature due to the alkalinity of the catalyst. Thus, repeated washing of the product is needed to make sure that the catalyst can be properly cleansed off from the final product.

In addition, it is also impossible to re-activate the used catalyst (Sreeprasanth *et al*., 2006) and this may lead to a concern of the disposal of this corrosive catalyst which may cause problem to the environment. Moreover, formation of soap by-product in the final product can be observed when high alkalinity homogeneous catalysts alkalinity were used (Sreeprasanth *et al*., 2006). This formation of soap by-product causes the separation process of the catalyst from the product becomes more difficult in addition to the catalyst separation which is in the same phase with the reactants.

Heterogeneous catalysts however, can be easily separated from the final product as they exist in different phase from the reactants. In this study, the catalyst appears to be in solid phase with the feedstock while the precursors for the reaction are in liquid phase. Separation can be done either through centrifugation, or simply by using filter paper with the help of suction due to high viscosity of the final product. With this approach, loss of product can be overcame with no repeated washing of final product and thus they can be considered as more environmentally friendly as compared to homogeneous catalysts. The advantages of using heterogeneous catalyst can also be seen in the research done by Chang *et al.* (2012) and Masood *et al.* (2012) where calcium methoxide catalyst was used.

The scope of this study includes producing a heterogeneous catalyst that has basic nature for the transesterification of POME and TMP to produce TMPTE. Mixed oxides of calcium and strontium from group II alkaline earth were synthesised to be studied, with strontium oxide as the varying compound with wt% of 5, 10, 15 and 20. Followed by the characterisation of the mixed oxides catalysts with analysis such as XRD, BET, TPD-CO_2, FESEM and SEM-EDX in order to obtain the physicochemical properties of the catalysts for the transesterification reaction. Last but not least, the final product will be analysed using GC-FID to determine the wt% yield of TMPTE and FT-IR for functional group determination of the final product.

1.3 Objectives of Study

The objectives of this study are:

1. To synthesize a heterogeneous mixed oxides base catalysts of CaO•xSrO that is suitable for the production of TMPTE;
2. To characterize the synthesised CaO•xSrO catalysts for their activity towards transesterification of POME with TMP to produce TMPTE;
3. To determine the optimised reaction conditions for the production TMPTE using the synthesised CaO•xSrO catalyst.

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