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DEVELOPMENT OF FOOD GRADE GREEN LUBRICANT FROM PALM OIL METHYL ESTER

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By

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DEVELOPMENT OF FOOD GRADE GREEN LUBRICANT FROM PALM OIL METHYL ESTER

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July 2015

Chairman : Robiah Yunus, PhD
Faculty : Engineering

Food grade lubricant is compulsory in food processing industry when there is a possibility for the lubricant to come into contact with a food product. Mineral-based oil is not safe and may contaminate food after contact. However, the commercially available food grade lubricants are expensive. In this study, the potential of using pentaerythritol ester as the base oil in the food grade lubricant was investigated. The synthesis of pentaerythritol ester was conducted using the transesterification process between palm oil methyl ester (PME) and pentaerythritol (polyol) producing pentaerythritol ester with mostly tetra ester structure. The optimization process of the transesterification reaction was assisted by response surface methodology (RSM) - central composite rotatable design (CCRD). Four factors were studied; temperature (140 - 190˚C), catalyst amount (0.5 – 1.5 wt % w/w), PME-to-pentaerythritol molar ratio (4:1 – 5:1) and duration (1 – 5 hr) to produce the maximum amount of pentaerythritol tetra ester. The optimum operating conditions were at 158˚C, catalyst amount 1.19%, molar ratio 4.5:1 and 1 hour reaction duration resulted in 40.13% of tetra ester. Additives approved by Food and Drug Administration (FDA) and United State Department of Agriculture (USDA) such as antioxidant (Irganox L 57), anti-wear (Irgalube 349) and corrosion inhibitor (Irgamet 39) were added at different composition and combination to enhance the base oil properties. Four formulated pentaerythritol esters were tested for oxidative stability test, four-ball test, and flash point test, of which the results showed comparable characteristics with a commercial chain lubricant. Acute toxicity test was also carried out to prove that the pentaerythritol ester is non-toxic. Among the formulated oils, a sample name Anti Wear Corrosion Inhibitor (AWCI) which comprised of 0.15 % Irgalube 349, 0.15 % Irgalube TPPT, and 0.1 % Irgamet 39, was chosen as the best formulation. AWCI exhibits high flash point, has better oxidative stability and excellent wear properties.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Sarjana Sains

PEMAJUAN PELINCIR HIJAU BERGRED MAKANAN DARIPADA METIL ESTER MINYAK SAWIT

Oleh

NUR ATIQAH MOHAMAD AZIZ

Julai 2015

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Pelincir bergred makanan adalah penting bagi industri pemprosesan makanan kerana terdapat kebarangkalian pelincir tersebut tertumpah pada produk makanan. Pelincir daripada mineral adalah tidak selamat dan mencemarkan makanan apabila berlaku pertumpahan ke atasnya. Walau bagaimanapun, pelincir bergred makanan komersial yang terdapat di pasaran adalah mahal. Penyelidikan ini mengkaji potensi kegunaan pentaerythritol ester sebagai asas minyak pelincir bergred makanan. Sintesis pentaerythritol ester dijalankan melalui proses transesterifikasi antara metil ester minyak sawit (PME) dan pentaerythritol (polyol) untuk menghasilkan pentaerythritol ester dengan komposisi tetra ester yang maksimum. Proses yang optimum bagi tindak balas transesterifikasi dibantu oleh kaedah permukaan gerak balas (RSM) – reka bentuk putaran komposit pusat (CCRD). Empat faktor yang telah dikaji adalah suhu (140 - 190˚C), kuantiti pemangkin (0.5 – 1.5 wt % w/w), nisbah PME kepada pentaerythritol (4:1 – 5:1) and tempoh masa (1 – 5 jam) bagi penghasilan pentaerythritol ester yang paling banyak. Keadaan operasi yang optimum adalah pada suhu 158˚C, dengan kuantiti pemangkin 1.19%, nisbah molar 4.5:1 and tempoh tindak balas selama 1 jam telah berjaya menghasilkan sebanyak 40.13% tetra ester. Bahan tambahan yang dibenarkan oleh Food and Drug Administration (FDA) dan United State Department of Agriculture (USDA) seperti anti pengoksidaan (Irganox 57), anti haus (Irgalube 349) dan pencegah karat (Irgamet 39) ditambah dengan komposisi dan kombinasi yang berbeza untuk mempertingkatkan ciri-ciri asas minyak. Empat formulasi pentaerythritol ester telah diuji dengan ujian kestabilan pengoksidaan, ujian four-ball, dan ujian takat kilat yang mana keputusannya menunjukkan ia setara dengan ciri-ciri pelincir rantai komersial. Ujian toksik akut juga telah dijalankan bagi membuktikan bahawa pentaerythritol ester adalah tidak toksik. Daripada minyak-minyak yang telah diformulasikan, satu sampel yang diberi nama Anti Wear Corrosion Inhibitor (AWCI) yang terdiri daripada 0.15 % Irgalube 349, 0.15 % Irgalube TPPT, dan 0.1 % Irgamet 39, telah dipilih sebagai formulasi terbaik dengan menunjukkan takat kilat yang tinggi, mempunyai kestabilan pengoksidaan yang lebih baik dan ciri-ciri tahan haus yang cemerlang.

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I certify that a Thesis Examination Committee has met on 14 July 2015 to conduct the final examination of Nur Atiqah binti Mohamad Aziz on her thesis entitled "Development of Food Grade Green Lubricant from Palm Oil Methyl Ester" 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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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AOAWCI	Anti Oxidant Anti Wear Corrosion Inhibitor
AOCS	American Oil Chemists' Society Method
AWCI	Anti Wear Corrosion Inhibitor
ASTM	American Standard Testing Method
BHT	Butylated Hydroxy Toluene
CCRD	Central Composite Rotatable Design
CFR	Code of Federal Regulation
CL	Commercial Lubricant
CoF	Coefficient of Friction
DSC	Differential Scanning Calorimeter
EHL	Elastrohydrodynamic
FDA	Food and Drug Administration
FID	Flame Ionization Detector
GBP	British Pound Sterling
GC	Gas Chromatography
IP	Institute of Petroleum
NPG	Neopentyl Glycol
NSF	National Sanitation Foundation
PE	Pentaerythritol
PEE	Pentaerythritol Tetra Ester
PME	Palm Oil Methyl Ester
PKOME	Palm Kernel Oil Methyl Ester
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
TMP	Trimethylolpropane
TOST	Test for Oxidative Stability of Steam Turbine Oils
USDA	United State Department of Agriculture
OECD	Organization for Economic Co-operation and Development
VI	Viscosity Index
WSD	Wear Scar Diameter

LIST OF SYMBOL

k	Number of Independent Variables
b_0, b_i, b_{ij}	Regression Coefficient
ρ	Density
υ	Kinematic Viscosity
η	Dynamic Viscosity
μ	Coefficient of Friction
α	Pressure Viscosity Coefficient
λ	Film Thickness Ratio
σ	Average Surface Roughness

CHAPTER 1

INTRODUCTION

1.1 Background

Lubricants are widely used in many industries; food, oil and gas, automotive, milling and others. They play important role in helping machinery to work effectively and smoothly since machinery movement involves friction between surfaces, wear and overheating (Moon, 2007). In food processing industry, lubricants are used mainly in chain conveyor, gear boxes, grinders, oven chain, can seamers, pump and hydraulic system (Moon, 2007). Because of the possibility that the lubricant may come in contact with the product, the most important criteria in lubricant selection is its effect on product consumer's healthiness. Food and Drug Administration Agency, US (Judge, 2004) has reported many cases of product withdrawal due to lubricant contamination such as the recall made by the Coca Cola Bottling Company, Maspeth, New York. On October 9^{th}, 1990, due to product contamination by a conveyor lubricant (Dicolube PL), the company had to recall 4,000 cases of Diet Coke and Sprite, packed in cans packages. Other incident happened in Hiroshima Japan (2002) where a company that manufacture product seasonings, lost almost GBP 1.1 million when 55 tons of Furkake seasoning was contaminated with a mineral lubricant of the hydraulic cylinder in the cutter.

In 2017, the lubricant consumption is expected to grow 43.6 million metric per ton due to excessive industrialization and growth of vehicle industry (Zulkifli *et al.* , 2014a). Most of the countries recuperate from the economic recession in 2009. Increasing demand of lubricant provides market opportunities of lubricant oil. Most of the world wide lubricants are produced from petroleum base oil. Despite the increase in global consumption of oil in the last 10 years, the oil production fluctuated and some countries even produced much less than expected (Bp, 2014). In Malaysia, oil production dropped from 739 to 716 barrels per year in 2009 and 2010, respectively, while the consumption increased 538 to 556 barrels per year respectively. This alarming worldwide depletion of petroleum reserves, leads to shift from petroleum based to other base stocks (Campanella *et al.* , 2010). Petroleum or mineral oils-based lubricants are considered to be harmful to human being and environment. Its toxicity and poor biodegradability can lead to health's problem and pollution (Willing, 2001; Aluyor and Ori-Jesu, 2009). Some of the lubricants might penetrate into the soil or vaporize into the air in case of spillage (Nagendramma and Kaul, 2012). Bartz (1998) reported that, almost 12 million tons of lubricants were circulated back to the environment annually based on application of lubricants. In Germany almost 50% of lubricant sold in the market is lost to environment (Regueira *et al.* , 2014).

Nagendramma and Kaul (2012) reported that there are three main groups of lubricants, mineral oils, synthetics lubricant and vegetable oils. Synthetic based lubricants may consist of either highly unsaturated or high oleic vegetable oils (HOVOs), low viscosity polyalphaolefins (PAOs), polyalkylene glycols(PAGs), dibasic acid ester (DEs) and polyol esters (PEs). Due to their excellent performance, the price of synthetic esters is much higher to mineral oil. However, the demand for synthetic ester is much higher to mineral based lubricants. Neopentyl polyol ester has more potential as compared to other ester due to its excellent thermal and oxidative stability, good lubricity, better viscosity, viscosity index and biodegradability (Yunus *et al.* , 2005; Chang *et al.* , 2012; Hamid *et al.* , 2012; Masood *et al.* , 2012; Padmaja *et al.* , 2012; Kamalakar *et al.* , 2013; Koh *et al.* , 2014). Vegetable oils are well-known for its biodegradability characteristic, and they are more favourable, as compared to petroleum-based oil lubricant. Vegetable oil-based lubricant is much cheaper in price relative to synthetic lubricant (Nagendramma and Kaul, 2012). Previously, castor beans, palm oil, soybean oil, and rapeseed oil have been used as the base oils (Linko *et al.* , 1997; Nagendramma and Kaul, 2012).

Since 1950s, various studies on pentaerythritol ester has been attempted by many researchers, however, limited information is available on the synthesis of aliphatic pentaerythritol ester as a lubricant. Bohner *et al.* (1962) reported the minimum viscosity-temperature coefficient for polyols. Niedzielski (1976) studied the bulk property optimization of neopentyl polyol ester as lubricants. According to Niedzielski (1976), polyol functionality has marked effects on the bulk properties compared to the number of carboxylic acids. Sosulina *et al.* (1980) studied the mass spectrometry of pentaerythritol ester and showed thermal stability due to its reactivity with synthetic fatty acids. Besides, Kyazimova (2008) also studied the thermally stable lubricants made from pentaerythritol and synthetic fatty acid using additives. The sample can resist up to 225˚C for 50 hours in the presence of copper, steel and aluminium before it was oxidized. Another study was made on the structure of neopentyl polyol ester and their lubricating properties. Eychenne and Mouloungui (1998) examined the viscosity, viscosity index and pour point. In that study, the authors used erucic acid from rapeseed ester and crambe oils as starting materials. They also supported previous work (Bohner *et al*., 1962; Niedzielski, 1976) regarding the number of functional group, where stability was increased with less number of remaining hydroxyl group. In other word, tetraester with no free hydroxyl group is expected to have the most stable structure.

From various studies on pentaerythritol ester application, none of them reports on the use of the ester as food grade lubricant. Another issue observed is that, no attempt was made to synthesize pentaerythritol ester using palm oil methyl ester as base oil. In line with developing a food grade lubricant, palm oil methyl ester has a big potential for lubricant industry due to palm oil availability, non-toxicity, and biodegradability. Furthermore, Malaysia has the second largest palm tree plantation in the world. Therefore using the raw material already-available in the country can contribute to economic development. Previous studies showed that transesterification of a polyol namely trimethylolpropane (TMP) with palm oil methyl ester (Uosukainen *et al.* , 1998; Yunus *et al.* , 2003a, 2003b; Yunus *et al.* , 2004) enhanced its lubricating properties. However, the viscosity of TMP triester is under 50 cSt. Hence, this study focused on the development of a new ester that has higher viscosity suitable for food grade lubricant and biodegradable. Polyol of pentaerythritol (PE) with four hydroxyl groups and methyl ester from palm oil were selected as starting materials. Tetra ester from pentaerythritol with no -OH group is expected to exhibit not only high viscosity lubricant but excellent lubricating properties. The effect of temperature on wear and friction performance of lubricant produced was studied to obtain further understanding on its characteristic. To make sure that the newly developed pentaerythritol ester is a food-grade and safe to consumers, an acute oral and toxicity tests were conducted on the formulated lubricant.

1.2 Objectives

1. To synthesize palm oil-based polyol ester and optimize the process conditions using response surface methodology (RSM).
2. To formulate food grade lubricant using palm oil–based pentaerythritol ester and to analyze its properties.
3. To investigate the effect of temperature on wear and friction performance of the formulated palm oil–based pentaerythritol ester.

1.3 Scope of Work

The scope of study of this research is to produce high performance food grade chain lubricant using palm oil methyl ester and pentaerythritol as starting materials. Sodium methoxide (alkaline catalyst) was selected as the catalyst because it can produce higher yield as compared to acid catalyst. The usage of palm oil methyl ester is preferred due to the availability of palm oil in Malaysia. There are many operating parameters affecting the synthesis of pentaerythritol esters such as temperature, amount of catalyst, reactant molar ratio and pressure. The optimization of these parameters by Response Surface Methodology was conducted to determine the best combination of factors which produced the highest yield of pentaerythritol tetra ester. Base oil properties of the pentaerythritol esters were measured such as density, colour, kinematic viscosity and moisture content and compared to the commercial base oil. The oxidative stability of base oil was enhanced with the addition of antioxidant and evaluated using the oxidative stability test as proposed by the American Standard Test Method (ASTM). Besides, anti-wear and corrosion inhibitor were also added to improve the lubricity and corrosive protection ability of the lubricant.

The properties of formulated lubricants were then tested using ASTM standard methods. Among the properties selected in this study were kinematic viscosity, flash point, four-ball test and then compared with a commercial lubricant. The effect of temperature on wear and friction of the formulated lubricant was also carried out based on the study conducted by (Zulkifli *et al.*, 2014a). The different oils were tested namely the pentaerythritol ester base oil, formulated pentaerythritol ester-based lubricant, and commercial lubricant. The wear and friction study provides information on lubrication regime, coefficient of friction and wear scar diameter.

The produced lubricant base oil was then characterized using Gas Chromatography. The amounts and types of additives used in the lubricant formulation were varied to get the best lubricant formulation with excellent lubricating properties. Further study on the effect of temperature to wear and friction of oil performance was also conducted. The newly formulated food grade green lubricant was also tested using industry standard tests and later compared with commercial lubricant.

1.4 Thesis Outline

This report consists of five chapters; first chapter comprises the background of the study, problem statement for the project, the objectives and the scopes of work. Next, Chapter 2 provides the literature review on lubricants, lubricant base oils, and modification of base oil to improve the base oils. Transesterification process for producing palm oil-based polyol ester is reported for at various reaction conditions, followed by introduction of additives used in the lubricant formulation at the end of Chapter 2.

Chapter 3 discusses the Response Surface Method used to optimize the reaction conditions for the synthesis of pentaerythritol ester. The analysis of base and the formulated oils using standard methods were also discussed. In chapter 4, the results of optimization, lubricant formulation and characterization of the lubricant as well as wear and friction studies are presented. Finally, conclusion is made and recommendation for the future work is proposed in the last chapter.

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