UNIVERSITI PUTRA MALAYSIA

BATCH PRODUCTION OF TRIMETHYLOLPROPANE ESTER FROM PALM OIL AS LUBRICANT BASESTOCK

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirement for the degree of Master of Science

DEDICATED TO

MUMMY AND DADDY, with love

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman : Associate Professor Robiah Yunus, PhD

Faculty : Engineering

The batch production of trimethylolpropane ester from palm oil as lubricant basestock was performed in 10 liters mini pilot batch reactor incorporated with high vacuum pump. This study has examined the optimum operating conditions in order to obtain the maximum level of production yield in a minimum time or minimum cost.

The experiments were carried out to synthesize palm oil based trimethylolpropane ester via chemical reactions in batch mode. The experiments focused on the effects of variations in the 1) temperature, 2) vacuum pressure, 3) molar ratio, 4) amount of catalyst and 5) speed of agitation. The chemical compositions of samples were analyzed via gas chromatography. The final products were tested for their lubrication properties such as TAN (Total Acid Number), kinematic viscosity, viscosity index (VI), wear and friction test.

Approximately 5 liters of trimethylolpropane ester from palm oil containing 86 w/w% of triester was successfully synthesized in two hours of operation. The optimal reaction conditions for mini pilot batch reactor were found to be as follows; 1) temperature: 120°C, 2) pressure: 20 mbar, 3) molar ratio: 3.8:1 (POME to TMP), 4) catalyst: 0.9 w/w% 5) speed of agitation: 180 rpm.

The kinetics data obtained from the laboratory scale experiment was successfully applied to the mini pilot batch reactor to estimate the yield of triester. As a conclusion, the study has proven that the synthesis method to produce trimethylolpropane ester from palm oil as a lubricant basestock developed in the laboratory (one liter) can be scale up to a mini pilot batch reactor (10 liters) with marginal effect on the reaction yield.

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

PENGHASILAN KELOMPOK ESTER TRIMETILPROPANA DARI MINYAK SAWIT SEBAGAI BAHAN ASAS MINYAK PELINCIR

Oleh

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Mei 2006

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Penghasilan kelompok ester trimetilolpropana dari minyak sawit sebagai bahan asas minyak pelincir telah dilaksanakan dengan menggunakan reaktor kelompok berskala mini pandu (10 liter) yang dilengkapi dengan vakum pam berkuasa tinggi. Kajian terhadap keadaan tindak balas optima juga telah diselidik bagi memastikan penghasilan produk yang berkualiti tinggi pada masa dan kos yang minimum.

Ester trimetilolpropana dari minyak sawit telah dihasilkan melalui proses tindakbalas kimia berkelompok. Ujikaji tertumpu keatas pelbagai kesan seperti 1) suhu; 2) tekanan vakum; 3) nisbah mol; 4) kuantiti pemangkin; 5) kelajuan pengaduk. Komposisi kimia hasil produk ini dianalisa dengan menggunakan gas kromatografi. Sifat-sifat pelincir bagi hasil produk ini seperti TAN (Nombor keasidan), kelikatan kinematik, kelikatan indek, kehausan dan geseran juga telah diuji.

Anggaran 5 liter ester trimetilolpropana dari minyak sawit telah berjaya disintesis dalam masa dua jam beroperasi. Tindakbalas optima bagi reaktor kelompok berskala mini pandu ini adalah seperti berikut:- 1) suhu:120°C; 2)tekanan vakum:20 mbar; 3) nisbah mol: 3.8:1 (POME:TMP); 4) kuantiti pemangkin: 0.9 w/w%; 5) kelajuan pengaduk:180 rpm.

Data-data kinetik yang diperolehi daripada ekperimen berskala makmal juga telah berjaya digunakan ke atas reaktor kelompok berskala mini pandu untuk menganggar hasil triester. Kesimpulannya, kajian ini telah berjaya membuktikan bahawa kaedah sintesis berskala makmal bagi penghasilan ester trimetilolpropana dari minyak sawit sebagai bahan asas minyak pelincir boleh diaplikasikan pada reaktor kelompok berskala mini pandu (10 liter) tanpa memberi kesan negatif terhadap hasil tindakbalas.

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LIST OF ABBREVIATIONS

$MW_{mixture}$	Molecular weight of mixture
MW_{TE}	Molecular weight of triester
C_A	Concentration of component A at any time
C_{AO}	Initial concentrations of component A
CPO	Crude Palm Oil
CSTR	Continuous Stirred Tank Reactor
DE	Diester
f_i	Feed rate (mol/s or kg/s)
F_{io}	Molar flow rate
k_3	Reaction rate constant for reaction 3
ME	Monoester
N_{im}	Moles of component i
N_{TE}	Moles of triester
PKO	Palm Kernel Oil
PME	Palm Oil Methyl Ester
r_i	Rate of reaction for component i
RME	Rapeseed Methyl Ester
RPM	Rotational per minute
t	Time (s or minute)
TE	Triester
TMP	Trimethylolpropane
TMPE	Trimethylolpropane Ester
V	Volume (m^3)
x_i	Fraction of i converted
$\rho_{mixture}$	Density of mixture
τ	Space time
υ	Volumetric flow rate (m^3/s)

CHAPTER 1

INTRODUCTION

In general, a lubricant comprises of two components, base oil and additive. Base oil is the major component in lubricating oil. It typically represents 90% of the finished product. Most lubricant base oils can be divided into three categories: mineral, synthetic or vegetable oil. Mineral base oils are mixtures of a wide range of hydrocarbons which are derived from various types of crude oils. Mineral oil base lubricants are blends of these mineral base oils with additives to enhance specific desired properties of mineral base oil or to suppress certain undesired characteristics. However, these products are usually toxic and not readily biodegradable. Thus, any accidental spillage of lubricant onto soil or river could contribute to an adverse impact to the environment and consequently harmful to plant and wildlife. The awareness and concern over the impact of mineral oil based lubricants on the environment have created an opportunity to produce environmentally acceptable lubricants from vegetable oils (Nelson, 2001; Hill, 2000).

The idea of using vegetable oil as lubricant base oil is not new. In fact, during the Second World War, vegetable oil was the second source of base oil due to the shortage of mineral oil. Vegetable oils have a number of inherent qualities that give them advantages over mineral oils as the base oil for lubricant. Unfortunately they are limited by their poor low temperature fluidity and poor oxidative stability at high temperature. The most desirable oil for lubricant is base oil with a high percentage of monounsaturated fatty acid, moderate amount of polyunsaturated fatty acid and low amount of saturated fatty acid. However, these limitations could be overcome by genetically engineered base oils and lubricant additives. Synthetic esters on the other hand have more desirable properties because they can be tailored made by careful selection of fatty acids and alcohol to give the desired properties (Yeong et al., 2004).

The development of synthetic esters in lubricant started in the 1930s in the United States and Germany. Synthetic esters include monoester, diester, polyol esters, fatty acid esters and complex esters. The raw materials for synthetic esters include straight or branched chain fatty acid with 6 to 18 carbons. These fatty acids can easily be obtained from vegetable oils such as palm, palm kernel, coconut, castor and tall oil and animal tallow. The diesters and polyol esters exhibit better viscosity indices, lower pour point and high flash points than mineral oil. These properties are desirable for the formulation of high performance lubricants. Recently, the fatty acid esters of neopentyl polyol, pentaerithrityl tetraheptanoate and coco fatty acid of trimethylolpropane ester are applied for automobile engine oil, Type II aviation turbine oils, hydraulic fluids, metal working lubricant and grease (Carceller, 2000; Bondioli, 2000).

The interest in the bio-lubricants derived from renewable resources like vegetable oil is growing due to their biodegradability, low toxicity and environmentally benign nature. Many European countries especially Germany, Switzerland, Austria and Scandinavia are leading the world to advance bio-lubricants to the markets through development and legislation. In Europe, the current bio-lubricants market is about 110,000 tons or approximately 2% of the total lubricants volume and is growing rapidly at 10% per annum (Kodali, 2002). The total production of vegetable oil around the world is also growing approximately doubling the volume for every 25 years. However, advance in chemistry, catalyst and bio-reactor design will begin to change this percentage. There is a consensus that in future, the demand will increase up to 75% because of the need to develop vegetable oil-based lubricants with higher performance characteristics (Bondioli and Igartua, 2000).

In Malaysia, vegetable oil based lubricant industry is quite young. However it has made tremendous progress in the last five years. One of the successful development which was achieved by Yunus and co-worker from Universiti Putra Malaysia, is on the synthesis of palm-based trimethylolpropane (TMP) esters as a lubricant base oil. The new class of bio-lubricant showed a good potential for various applications such as hydraulic fluids, metalworking fluids and general lubricating oil. It also shares most of the salutary properties of other vegetable oils as lubricants such as high viscosity index, good lubricity, high flash point, and low temperature characteristic.

Vegetable oil-based polyol esters have been produced in various ways from fatty acid and fatty acid methyl ester. Currently, palm oil methyl esters are assuming an increasingly important role as starting materials in the oleochemical industry. Methyl esters are reportedly superior to fatty acid for producing a number of fatty acid derivatives. Their production cost is also more competitive owing to lower capital and energy cost. Consequently, palm-based methyl esters (PME) were chosen as starting materials in the synthesis of polyol esters as lubricants. The polyol selected was trimethylolpropane (TMP), as it is branched and has a relatively low melting point. The experimental were conducted in laboratory scale to produce a high performance and environmentally friendly lubricant based oil from palm oil (Yunus et al., 2003; Henderson and Osborne, 2000).

However this lubricant was not readily available for commercial testing due to limited production volume. Thus based on previous worked, this study will concentrate on producing a large volume of palm based polyol ester. In order to increase the amount of production, the experiments were carried out using a mini pilot batch reactor incorporated with a high vacuum pump. The operating conditions were varied within the range used in previous work carried by Yunus et al. (2003). The optimum conditions were derived based on the chemical and physical properties of the final products obtained from the reactions.

This study dealt with real problems in a batch lubricant production and provides a unique insight into multi product batch processing and its special problems. In particularly, the thermal history of the chemicals will affect the product quality and also reduced the effective batch capacity. Therefore, it is necessary to understand the mechanisms which lead to these changes so that the effects caused by the equipment and operating methods can be separated from the chemistry of the process (Yates, 1997).

1.1 Objective and Scope of Work

The objectives of this research project are:-

1. To produce palm-based trimethylolpropane ester using 10L reactor.
2. To optimize the operating conditions.
3. To evaluate the lubricating properties of the palm-based trimethylolpropane ester.

The scopes of work are directed towards studying the effects of operating parameter such as temperature, vacuum pressure, molar ratio, catalyst amount and agitator speed on the reaction conversion. A number of experiments were performed in a mini pilot batch reactor incorporated with a vacuum pump in order to obtain the optimum production yield. The final product was separated from the unwanted materials firstly by the gravitational settling and followed by the vacuum distillation to remove the unreacted palm oil methyl ester. The end products were tested for their lubrication properties such as kinematic viscosity, viscosity index, total acid number (TAN) as well as wear and friction tests.

1.2 Thesis Outline

This thesis contains five chapters. The first chapter contains a general introduction and background of the thesis as well as the objective and the scope of work. Chapter 2 consists of several previous research works on lubricant base oil and related areas. It also covers the review of literature of palm oil based products and their potential usage. The discussion on chemical reactor is also included in this chapter. Chapter 3 presents the research methodology and describes the equipment used in this study. Chapter 4 presents the results obtained from the experiments. In addition, the chapter includes the discussion of the results as well as the physical and chemical properties of palm-based TMP esters obtained from the properties tests. Finally, Chapter 5 summarizes and concludes the research that had been carried out in this study. Lastly, the future work is suggested at the end of the chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Vegetable oils have a number of inherent qualities that give them advantages over petroleum oils as the feedstock for lubricants. Unlike mineral oils, which can persist in the environment for years, vegetable oils are readily biodegradable. Vegetable-based lubricants can be derived from a range of vegetable oils and are inherently biodegradable and low in toxicity and do not harm aquatic organisms. These qualities are particularly important for lubricants used in environmentally sensitive areas such as marine ecosystem and for those with a high potential of being lost to the surrounding environment. However, this industry is still in the development stage, thus it shows the current market share is low. Frost and Sullivan, a marketing analyst group, places it at less than one percent of the U.S market (Yamada, 2005; Nelson, 2001).

Currently, numerous vegetable oils from various sources such as canola, sunflower, soybean and palm are used in lubricant applications. For instance, the lubricant's application include additive in synthetic oil, two cycle-motor oils, chain oils, hydraulic oils, greases, bio diesels (Lawate et al., 2005). In North America, sixteen types of lubricant, hydraulic fluid and grease have been commercialized using soybean as well as canola oil. Now a day, rapeseed (canola) oil is the most widely used vegetable oil and has dominated the lubricant market due to its relatively good oxidative stability, it reasonable cost and its wide availability in both Europe and North America. Even though, soy-based lubricants are less expensive than canola, but do not perform very well. However, researcher efforts are under way to develop varieties that can meet performance standards of rapeseed / canola (Ashmeed, 2002; Bondioli et al., 2000; Lubrizol Corporation). In India, coconut oil has been used as alternative base oil for automobile lubricant. The new invention which was presented by Jayadas from Cochia University of Science and Technology (CUSAT) has also been tested to two stroke engine. An environmental evaluation of coconut oil as lubricant revealed that it consumed low energy, generated hardly any waste material and has no emission (Kurian, 2004).

2.2 Vegetable Oil-Based Lubricants

Vegetable oils are important renewable resources compared to fossil and mineral raw materials. The sources of oils and fats are various vegetable and animal raw materials (e.g., tallow, lard) with the vegetable raw materials soybean, palm, rapeseed and sunflower oil being the most important (Hill, 2000). Some of their common uses prior to 1939 are listed in Table 2.1 (Odi-Owei, 1988).