UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF PALM-BASED TRIMETHYLOLPROPANE ESTERS AND THEIR POTENTIAL USE AS LUBRICANT BASESTOCK

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By

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The synthesis of new palm based polyol esters as the biodegradable base stock for lubricant production was conducted via chemical transesterification of palm based methyl esters with trimethylolpropane, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP). Both palm oil (POME) and palm kernel methyl esters (PKOME) were used as the starting materials and sodium methoxide as the catalyst. The reactions were carried out under different temperatures (80 to 140°C) and vacuum pressures (0.1 to 500 mbar). Palm based TMP esters containing 98% w/w triesters was successfully synthesized in 45 minutes under 10 mbar vacuum, T=120°C, and 3.9:1 molar ratio of POME to TMP. While the effect of methyl esters to TMP ratio was minimal, the optimum molar ratio was found at 3.5:1 and 3.8:1 in palm kernel and palm oil TMP ester synthesis respectively. The amount of catalyst required was less than 1.0% w/w of the total mass of reactants. The optimal reaction conditions were: temperature, 130°C for POME and 120°C for PKOME; vacuum, 20 mbar; catalyst, sodium methoxide at 0.7% (w/w); POME:TMP, 3.8:1; PKOME:TMP, 3.5:1; duration, 1 hour. Analysis of the reaction products was performed using GC with a

high temperature capillary column, SGE HT5 operated at a temperature gradient of 6°C/min starting from 80°C to 340°C. Before injection, the sample was derivatized with N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) in ethyl acetate at 40°C for at least 10 min. This procedure provided a complete separation of the reaction products: TMP, palm based methyl esters, monoesters, diesters and triesters.

The kinetics study on transesterification of palm oil-based methyl esters with TMP established that the reactions occurred via three stepwise and reversible elementary reactions. The reversible reactions were suppressed by applying large excess of methyl esters and continual withdrawal of methanol via vacuum. The optimum ratios for k_2/k_1 and k_3/k_1 in palm oil TMP esters synthesis ranged from 0.70-0.80 and 0.21-0.25 respectively. For palm kernel TMP ester synthesis, the ratios for k_2/k_1 and k_3/k_1 were between 0.60-0.70 and 0.12-0.15. The activation energies of the reactions ranged from 17.2 to 33.9 kcal/mol. The lubrication properties of palm oil-based TMP esters indicated good potential as base stock in biodegradable lubricant formulation. Despite its high pour points, other lubrication properties such as viscosity, VI, wear and friction properties are comparable to commercial hydraulic fluids. The pour point (PP) problem associated with the saturation level in palm oil was resolved, as the PP was successfully improved to –32°C in high oleic palm based TMP esters. However, lowering the PP has negative effect on oxidative stability as well as wear and friction. With proper additives, it is believed that the new formulated high oleic palm oil TMP ester will offer a wide variety of applications: hydraulic fluids, fire resistant fluids, metalworking fluids, and general lubricating oils. Its unique chemistry offers excellent oxidative and thermal stability, superior low temperature behaviour, and biodegradability.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS ESTER TRIMETILPROPANA MINYAK SAWIT DAN POTENSI PENGGUNAAN SEBAGAI BAHAN ASAS MINYAK PELINCIR

Oleh

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Pengerusi: **Profesor Madya Fakhru'l-Razi Ahmadun, Ph.D.**

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Sintesis ester poliol minyak sawit sebagai bahan asas dalam penghasilan minyak pelincir biodegradasi dijalankan melalui proses transesterifikasi kimia metil ester minyak sawit dengan trimetilolpropana, 2-etil-2-(hidroksimetil)-1,3-propanadiol (TMP). Metil ester dari minyak kelapa sawit (POME) dan dan minyak isirong kelapa sawit (PKOME) digunakan sebagai bahan mentah dan sodium metoksida sebagai pemangkin. Tindakbalas dijalankan pada suhu 80 ke 140°C dan tekanan vakum, 0.1 ke 500 mbar. Ester TMP minyak sawit yang mengandungi 98% w/w triester telah berjaya disintesis dalam masa 45 minit pada tekanan 10 mbar, suhu 120°C dan nisbah mol POME:TMP, 3.9:1. Walaupun kesan nisbah mol POME (PKOME):TMP keatas tindakbalas adalah minima, nisbah optima adalah 3.5:1 dan 3.8:1 bagi sintesis ester TMP minyak sawit dan isirong minyak sawit. Jumlah pemangkin yang diperlukan adalah kurang dari 1% dari jumlah jisim bahan tindakbalas. Keadaan tindakabalas optima adalah: suhu, 130°C bagi POME and 120°C bagi PKOME; tekanan: 20 mbar; pemangkin: sodium metoksida pada 0.7% (w/w); POME: TMP, 3.8:1; PKOME: TMP, 3.5:1; masa, 1 jam. Analisis hasil tindakbalas dibuat

menggunakan GC dengan turus kapilari bersuhu tinggi, SGE HT5 pada suhu berkala 6°C/min dari 80°C ke 340°C. Sebelum disuntik, sampel ditindakabalaskan dengan N,O-Bis(trimetilsilil) trifluoroacetamida (BSTFA) dalam etil acetat pada suhu 40°C selama 10 min. Kaedah ini membolehkan analisa kuntitatif kerana pemisahan lengkap hasil tindakabalas seperti: TMP, metil ester, monoester, diester dan triester.

Kajian kinetik keatas transesterifikasi metil ester minyak sawit dengan TMP menunjukkan tindakabalas berlaku secara turutan melibatkan tiga tindakbalas asas berbalik. Tindakbalas berbalik dikurangkan dengan menggunakan metil ester lebihan dan penyingkiran berterusan metanol melalui vakum. Nisbah optimum pekali tindakbalas k_2/k_1 and k_3/k_1 dalam sintesis ester TMP minyak sawit berada pada julat 0.70-0.80 dan 0.21-0.25. Bagi sintesis ester TMP minyak isirong sawit, nisbah k_2/k_1 dan k_3/k_1 adalah diantara 0.60-0.70 dan 0.12-0.15. Tenaga keaktifan tindakabalas bagi sintesis tersebut berada diantara 17.2 to 33.9 kcal/mol. Ujian pelinciran keatas ester TMP minyak sawit menunjukkan potensi tinggi minyak tersebut sebagai bahan asas dalam formulasi minyak pelincir biodegradasi. Walaupun takat tuang (PP) tinggi, kelikatan,indek kelikatan, ciri haus dan geseran adalah setara dengan minyak hidralik yang ada dipasaran. Masalah PP yang dikaitkan dengan tahap tepu minyak sawit telah dapat diselesaikan dengan penemuan baru, ester TMP minyak sawit oleik tinggi dimana PP dapat dikurangkan ke –32°C. Walaubagaimanapun, pengurangan PP menimbulkan kesan negatif kepada kestabilan oksida dan ciri haus serta geseran. Dengan penggunaan bahan tambah tertentu, minyak sawit oleik tinggi dipercayai dapat digunakan dalam pelbagai kegunaan: bendalir hidralik, bendalir logamkerja, dan minyak pelincir am. Ciri kimianya yang unik menawarkan kestabilan terma dan oksida yang tinggi, sifat suhu rendah yang baik dan biodegradasi.

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TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS/NOTATION/GLOSSARY OF TERMS

Abbreviations

DE	Diesters
DG	Diglycerides
FTIR	Fourier transform infrared refractometry
GC	Gas chromatography
HPLC	High pressure liquid chromatography
M	Methanol
MG	Monoglycerides
ME	Monoesters
PA	Polyol
PE	Polyol ester
PKOME	Palm kernel oil methyl esters
POME	Palm oil methyl esters
POTE	High oleic palm oil TMP esters
PKOTE	Palm kernel oil TMP esters
PPOTE	Palm oil TMP esters
TE	Triesters
TG	Triglycerides
TMP	Trimethylolpropane
TLC	Thin layer chromatography

Nomenclatures

C_A, C_B, C_C, and C_D	Concentrations of components A, B, C and D (mol/dm^3)
C	Average concentration of an adsorbed species (mol/dm^3)
C_m	Concentration corresponding to a complete formation of monomolecular layer on the catalyst surface (mol/dm^3)
C_v	Concentration of vacant sites (mol/dm^3)
[POME]	Composition of POME (wt %)
[ME]	Composition of ME (wt %)
[DE]	Composition of DE (wt %)
[TE]	Composition of TE (wt %)
E	Activation energy (cal/mol)
K	Equilibrium constant (dimensionless)
K_A	Adsorption equilibrium constant (dimensionless)
k_1, k_2, k_3	Reaction rate constants for reactions 1, 2, and 3 (wt^{-1}min^{-1})
k_1', k_2', k_3'	Reaction rate constants for reverse reactions 1, 2, and 3 (wt^{-1}min^{-1})
k_a	Rate constant for adsorption
k_a'	Rate constant for desorption
R_1	$\{[TMP_o]k_1k_2\}/R_2R_3R_4$
R_2	(k_2-k_3)
R_3	(k_1-k_3)
R_4	(k_1-k_2)
α	k_2/k_1

β	k_3/k_1
δ	$k_1/(k_1-k_2)$
ν	Kinematic viscosity, mm^2/s (cSt)
μ	Dynamic viscosity, mPa.s (cP)
ρ	Density (g/ml)
Subscript $_{A, B, C, D}$	Reacting components A, B, C and D
Subscript $^{i, j}$	ith or jth component
Subscript $_{o}$	Initial condition
Superscript $^{\alpha, \beta, \chi, \text{ and } \delta}$	Orders of reaction

CHAPTER 1

INTRODUCTION

1.1 Background

Biodegradable lubricants in the form of animal and vegetable fats and oils have been in use since ancient history. However, in the second half of the 20th century these natural lubricants are predominantly replaced by mineral-based lubricants due to its cost and performance considerations (Dowson, 1997). Despite its inherent limitations, natural fats and oils continued to play an important role in lubricant formulation. According to Formo (1982), about 10,000 tonnes (20 millions pounds) of fats and oils were used for lubricants production in 1962 and increased to 100,000 tonnes in 1976. The US Department of Agriculture has estimated about 54,000 tonnes (108 million pounds) of vegetable oils was used in lubricant formulations in 1993, out of 70 million tonnes of vegetable oils currently produced worldwide (Margaroni, 1999). This figure represents approximately 0.5% of total lubricants supplied to the US market. (Honory and Boeckendstedt, 1998)

Today, most of the lubricants and functional fluids are derived exclusively from petrochemical or mineral bases. They account for 85-90 % of the total world lubricants. Whilst, less than 15% of the world lubricants are synthetic-based, the synthetic-based lubricants offer high performance oil with superior lubricity, higher thermal stability, excellent oxidative stability, lower volatility, and hence fewer oil change requirement (Moore *et al*, 2003; Shanley and Butcher, 1999). Due to its poor oxidative stability, vegetable oil-based lubricants account for only 1% of total world lubricants. Adding additives such as antioxidant and pour point depressant enhances the properties of these biodegradable lubricants.

The awareness of preserving the environment has inspired research and development in environmental friendly products such as biodegradable lubricants. Lubricants are one of many hazardous contaminants of our environment, almost 90% are mineral-based and most of the used oils are not regenerated. It is reported that every year million tonnes of engine, industrial and hydraulic oils leak into the ground, waterways or are disposed off into the environment. It was calculated that up to 600,000 tons of oil a year disappear uncontrolled in the European Community (EC) alone (Wilson, 1998). According to the US Navy statistics, the total oil spilled in the US coasts is increasing alarmingly, from 17,370 gallons in 1990 to 66,404 in 1997 and up to 181,453 gallons in 1998 (Johnson, 1999).

The modern developments in high-performance biodegradable lubricants began only in the 1970's. The first biodegradable lubricant was two-stroke oil based on synthetic esters, which was commercially available in 1975. It was developed in response to the increasing environmental concern over the use of petroleum-based lubricants in environmentally sensitive areas and in once-through applications. Many large corporations such as Mobil Oil Co., BP, Castrol and Shell have formulated range of biodegradable products with specific applications. These products are available commercially and conformed to various categories of biodegradable lubricants classifications such as German's "Blue Angel" Eco-label (Hery and Battersby, 1998; Kiovsky *et al.*, 1994).

The most critical areas requiring biodegradable lubricants are the "total loss" or "once through" materials such as chain saw lubricants, two-cycle–engine oils, and hydraulics fluids (Kiovsky *et al.*, 1994). Due to the higher risks in entering soil and