EFFECTS OF PARTIAL ESTERS ON THE PROPERTIES OF PALM-BASED TRIMETHYLOLPROPANE ESTERS

By

ANITA BINTI ABU BAKAR

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

November 2006

DEDICATION

To my beloved husband Mohammad Johari, my son Imran Hadi and my parents

For understand and love….

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

EFFECTS OF PARTIAL ESTERS ON THE PROPERTIES OF PALM-BASED TRIMETHYLOLPROPANE ESTERS

By

ANITA HJ. ABU BAKAR

November 2006

Chairman: **Associate Professor Robiah Yunus, PhD**

Faculty: **Engineering**

Some concerns have been raised regarding the oxidative stability of vegetable oil-based fluids. Lack of oxidative stability will increase the rate of oxidation and degradation of the oil. Oxidation causes sludge and deposits formation, clogging of oil passages and corroding the equipment that they lubricate. Earlier findings have indicated that oxidative stability is partly due to the presence of partial ester in the lubricant. The hydroxyl group present in the partial ester increases the oxidative stability of the lubricant. Thus, a wide range of palm-based trimethylolpropane esters (TMPE), which contain different percentages of partial esters, were synthesized. The palm-based TMP esters (mono esters, diesters and triesters) were esterified from

palm oil methyl esters (PME) with trimethylolpropane [2-ethyl-2-(hydroxymethyl)-1,3-propanediol;TMP] and sodium methoxide (CH_3ONa) as catalyst.

Quantification of unreacted palm oil methyl esters (PME), monoesters, diesters, and triesters were performed using gas chromathography (GC), with a high temperature capillary column (SGE HT5), operated at a temperature gradient of 6 ^oC/min starting from 80 ^oC to 340 ^oC. The influence of operating variables (temperature, pressure, molar ratio PME:TMP and catalyst amount) on diester formation were studied and analyzed. Palm oil TMP esters containing 5 – 30 % (w/w) partial esters (monoesters and diesters) were successfully synthesized at different operating variables.

The effects of partial ester on lubrication properties were also studied. Hydroxyl group in partial esters can, under certain conditions, give a positive effect on lubrication properties such as viscosity and viscosity index, thermal oxidative stability and wear and friction. Kinematic viscosity of the TMP esters increases with the partial esters content. The optimum hydroxyl value (OHV) for thermal oxidative stability of the oils was observed at 27.2, while the optimum diesters (DE) %(w/w) in the oils for wear and friction characteristics was observed at 26.8 %(w/w), corresponding to the OHV value of 39.5.

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

KESAN-KESAN SEPARA ESTER TERHADAP SIFAT-SIFAT PELINCIRAN ESTER TRIMETILPROPANA MINYAK SAWIT

Oleh

ANITA HJ. ABU BAKAR

November 2006

Pengurusi : Profesor Madya Robiah Yunus, PhD

Fakulti : Kejuruteraan

Terdapat kebimbangan telah dikemukakan berkenaan kestabilan oksida minyak pelincir berasaskan sayuran. Kekurangan sifat kestabilan oksida akan meningkatkan kadar pengoksidaan dan penurunan minyak pelincir. Pengoksidaan menyebabkan, bahan enap cemar dan endapan terhasil, menjadikan laluan minyak tersumbat dan mengkakis peralatan yang dilincirkan. Penemuan terdahulu telah menunjukkan bahawa kestabilan oksida ini sebahagiannya disebabkan oleh kewujudan separa ester di dalam minyak pelincir. Kumpulan hidroksil yang wujud dalam separa ester itu telah meningkatkan kestabilan oksida minyak pelincir tersebut. Maka, perbagai rangkaian ester trimetillolpropana (TMPE) yang berasaskan minyak sawit yang

mengandungi peratusan separa ester (ester mono, ester dwiTMP dan ester triTMP) yang berbeza telah disentesiskan. Ester TMP minyak sawit telah diesterkan dari metil ester minyak sawit (PME) dengan trimetilpropana, [2-etil-2-(hidrosimetil)-1,3-propanadiol;TMP] dan sodium metoksida (CH_3ONa) bertindak sebagai pemankin.

Pengkuantitian sisa ester metil minyak sawit, monoester mono, dwiester dan triester dilakukan dengan menggunakan gas kromatografi (GC), dengan turus kapilari bersuhu tinggi (SGE HT5), dioperasikan pada suhu berkala 6^oC/min bermula dari 80^oC hingga 340^oC. Kesan pengaruh pembolehubah operasi (suhu, tekanan vakum, nisbah molar PME:TMP dan jumlah pemankin) keatas pembentukan diester telah dikaji dan dianalisiskan. Ester TMP minyak sawit yang mengandungi separa ester 5 – 30 %(w/w) (monoester and diester) telah berjaya disentisiskan pada pembolehubah operasi yang berbeza.

Kesan separa ester keatas sifat pelinciran telah dikaji. Hidroksil dalam keadaan yang tertentu boleh memberikan kesan yang positif keatas sifat-sifat pelinciran seperti kelikatan dan indek kelikatan, kestabilan oksidaa haba serta kehausan dan geseran. Kelikatan minyak pelincir meningkat dengan peningkatan kandungan separa ester di dalam minyak pelincir itu. Nilai hidroksil (OHV) yang optima untuk kestabilan oksida haba minyak pelincir adalah 27.2. Manakala peratus optima DE didalam minyak pelincir untuk sifat kehausan dan pelinciran yang baik adalah 26.8 %(w/w), iaitu yang mengandungi nilai OHV 39.5.

ACKNOWLEDGEMENTS

ALHAMDULILLAH, through His Blessings and Dignity of Allah s.w.t., this study was completed. I would first like to take this opportunity to express my sincere gratitude to my supervisor Associate Professor Dr. Robiah Yunus for her invaluable advice, tireless guidance and constant encouragement leading to the completion of this study. I also wish to thank the lecturers who served on my graduate committee; Associate professor Dr. Fakhrul-Razi Ahmadun and Dr. Luqman Chuah Abdullah. Their knowledge in a broad range of disciplines helped me gain a new perspective on biodegradable lubricant.

In addition to these lecturers, I am also indebted to the other students who have helped me in my work. Siti Zubaidah and Norhalaliza, with whom I have worked closely during my graduate program, have been capable colleagues as well as good friends. I also thank Encik. Joha, Encik. Tarmizi, Encik. Ismail and Puan Maslinda for their contributions to this research. My gratitude goes also to my friends who have provided all the moral support I could handle: Raja Izzawati, Azhari, Look Kar Yang, David, Christina and Sarina.

Most importantly, the understanding, patience and moral support of my husband, Mohammad Johari Jamaludin, my son Muhammad Imran Hadi and family are deeply appreciated.

I certify that an Examination Committee has met on 21th November 2006 to conduct the final examination of Anita Binti Abu Bakar on her Master of Science thesis entitled "Effects of Partial Esters on the Properties of Palm-Based Trimethylolpropane Esters" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Thomas Choong Shean Yaw, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Saari Mustapha, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Suraya Abdul Rashid, PhD
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Abdul Latif Ahmad, PhD
Professor
Faculty of Engineering
Universiti Sains Malaysia
(External Examiner)

_____
HASANAH MOHD. GHAZALI, PhD
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 15 FEBRUARY 2007

This thesis 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 are as follows:

Robiah Yunus, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Fakhru'l-Razi Ahmadun, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Luqman Chuah Bin Abdullah, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

_____
AINI IDERIS, PhD
Professor / Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or currently submitted for any other degree at Universiti Putra Malaysia or other institutions.

_____

ANITA BINTI ABU BAKAR
Date: 19 JANUARY 2007

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Term	Definition
β	Heating rate, (^{o}C/min)
A	Frequency factor (min^{-}1)
CoF	Coefficient of friction
DE	Diesters
DTA	Derivative thermal analysis
DSC	Differential scanning calorimetry
E_a	Activation energy (KJ/mol)
GC	Gas chromatography
HPDSC	High Pressure Differential Scanning Calorimetry
HPLC	High Performance Liquid Chromatography
IV	Viscosity index
ME	Methyl esters
OH	Hydroxyl
OHV	Hydroxyl value (mg KOH/g sample)
PME	Palm oil methyl ester
PP	Pour point
TAN	Total acid number
TE	Triesters
TGA	Thermogravimetric analysis

TMP	Trimethylol propane
TMPE	Trimethylolpropane esters
T_{on}	Onset temperature (^{o}C)
v	Kinematic viscosity, mm^2/s, (cSt)
WSD	Wear scar diameter