

**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

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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 chromatography (GC), with a high temperature capillary column (SGE HT5), operated at a temperature gradient of $6\text{ }^\circ\text{C}/\text{min}$ starting from $80\text{ }^\circ\text{C}$ to $340\text{ }^\circ\text{C}$. 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

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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

mengandung peratusan separa ester (ester mono, ester dwiTMP dan ester triTMP) yang berbeza telah disintesis. 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 $6^\circ\text{C}/\text{min}$ bermula dari 80°C hingga 340°C . Kesan pengaruh pembolehkan operasi (suhu, tekanan vakum, nisbah molar PME:TMP dan jumlah pemankin) keatas pembentukan diester telah dikaji dan dianalisis. Ester TMP minyak sawit yang mengandungi separa ester 5 – 30 % (w/w) (monoester and diester) telah berjaya disintesis pada pembolehkan 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 oksida 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.

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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:

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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

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LIST OF ABBREVIATIONS

Term	Definition
β	Heating rate, ($^{\circ}\text{C}/\text{min}$)
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 (°C)
v	Kinematic viscosity, mm ² /s, (cSt)
WSD	Wear scar diameter