



UNIVERSITI PUTRA MALAYSIA

***SYNTHESIS OF PALM OIL-BASED EPOXIDIZED
TRIMETHYLOLPROPANE ESTERS AS OXIDATIVELY
STABLE LUBRICANT***

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LUBRICANT**

By

FERRA NAIDIR

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

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April 2011

Chairman : Associate Professor Robiah Yunus, Ph.D

Faculty : Engineering

The main objective of this study is to improve the oxidative stability of trimethylolpropane ester (TMP ester) by modifying the unsaturated fatty acids structure of TMP ester through an *in-situ* epoxidation reaction. The *in-situ* epoxidation reaction of TMP ester was conducted to produce epoxidized trimethylolpropane ester (epoxidized TMP ester). The synthesis takes place by the reaction of a carboxylic acid (acetic acid: CH_3COOH) as the oxygen carrier with concentrated hydrogen peroxide (H_2O_2) as the primary source of oxygen to produce a percarboxylic acid (peracetic acid) as an epoxidizing agent. A small amount of sulfuric acid catalyst was used to speed up the reaction to form peracetic acid. The effects of CH_3COOH concentration, H_2O_2 concentration, temperature, reaction time and the catalyst were investigated to obtain the optimum yield of oxirane ring at 3.92%. The highest percentage of oxirane oxygen was obtained when the epoxidation was carried out using molar ratio of $\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ at 1 : 5.5 mol, 50 °C of

temperature, 2 h reaction time, and 2% (w/w) of catalyst. Fourier transform infrared (FTIR) spectra showed the formation of epoxy group at the wave number of 824 cm^{-1} .

A central composite design (CCD) technique was used to determine the optimum conditions for the epoxidation of palm oil-based TMP ester. Four independent variables were applied (concentration of CH_3COOH , concentration of H_2O_2 , temperature, and reaction time) to correlate with three responses (percentage of oxirane oxygen, iodine value, and hydroxyl value). The optimum values of percentage of oxirane oxygen, iodine value, and hydroxyl value were 4.01, 1.94, and 0.43%, respectively under the following operation conditions; 0.59 mol of CH_3COOH concentration, 7.5 mol of H_2O_2 concentration, temperature at 50 °C and reaction time of 7 h.

The kinetics of epoxidation of palm oil-based TMP esters was studied based on the assumptions of pseudo first order and second order mechanisms. The kinetic study was conducted to cover two regions of temperatures namely low temperatures region (30, 50, and 60 °C) and high temperature region (70, 80, and 90 °C). The rate constants for pseudo first order rate model for low and high temperatures in the range of 30-60 °C and 70-90 °C were $9 \times 10^{-4} - 5.5 \times 10^{-3}$ and $1.29 \times 10^{-2} - 2.09 \times 10^{-2} \text{ h}^{-1}$, respectively. The rate constants for second order rate model for low and high temperature regions were $1.3 \times 10^{-3} - 1.55 \times 10^{-2}$ and $0.03 - 8.37 \times 10^{-2} \text{ l mol}^{-1}\text{h}^{-1}$, respectively. The activation energies for second order model were 69.4 and 53.3 kJ mol^{-1} for low temperature and high temperature region respectively. The activation energies value indicated that the reaction easy to take place at high temperature.

The kinetics of oxidative degradation for epoxidized TMP ester, TMP ester, and commercial oil (cooking oil) was also investigated. This was carried out using differential scanning calorimetry (DSC) to analyze the rate of oxidation where the data was obtained at a heating rate of 5 °C/min. The result showed that the onset temperature for oxidation for both of TMP ester and cooking oil was at 170 °C while for epoxidized TMP ester, it was slightly higher at a temperature of 187 °C. The activation energy for oxidation was calculated using Ozawa Flynn Wall method where the values for epoxidized TMP ester, TMP ester, and cooking oil were 112.89, 78.28, and 75.45 kJ/mol, respectively. These results showed that the oxidative stability of TMP esters has been improved significantly by epoxidation of TMP esters. The lubrication properties of epoxidized TMP ester also indicated good potential as a base stock for lubricant formulation due to the marked improvement in lubricating characteristic compared to TMP ester. Although the pour point increased slightly but other lubrication properties are better than the properties of most vegetable oil-based commercial base oils.

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

**SINTESIS EPOKSIDASI ESTER TRIMETHYLOLPROPANE DARIPADA
MINYAK KELAPA SAWIT SEBAGAI MINYAK PELINCIR YANG STABIL
SECARA OKSIDATIF**

Oleh

FERRA NAIDIR

April 2011

Pengerusi : Profesor Madya Robiah Yunus, Ph.D

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Objektif utama dalam penyelidikan ini adalah untuk meningkatkan kestabilan oksidatif ester trimethylolpropane (TMP ester) dengan mengubah suai struktur asid lemak tidak tepu TMP ester melalui tindak balas epoksida secara *in-situ*. Tindak balas pengepoksidaan secara *in-situ* oleh TMP ester telah dijalankan untuk menghasilkan epoksida TMP ester. Sintesis itu terjadi dengan tindak balas oleh asid karboksilik (asid asetik: CH_3COOH) sebagai pembawa oksigen, dengan hydrogen peroksida yang pekat (H_2O_2) yang berfungsi sebagai sumber utama oksigen untuk menghasilkan asid perkarboksilik (asid perasetik) sebagai agen pengepoksidaan.

Sedikit pemangkin asid sulfuric telah digunakan untuk melancarkan tindak balas antara H_2O_2 and CH_3COOH untuk membentuk asid perasetik. Kesan-kesan kepekatan CH_3COOH dan H_2O_2 , suhu, masa tindak balas dan kesan pemangkin adalah diselidik untuk memperoleh hasil cincin oksirana yang optimum oleh peratus analisis oksirana oksigen di mana nilai ialah 3.92%. Peratus oksirana oksigen

tertinggi telah ditentukan apabila epoksidasi telah dijalankan menggunakan nisbah molar kepekatan dari $\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ pada 1 : 5 mol kepekatan, suhu pada $50\text{ }^\circ\text{C}$, masa tindak balas selama 2 jam, dan 2% (w/w) jumlah pemangkin. Jelmaan Fourier inframerah (FTIR) spektrum menunjukkan pembentukan kumpulan epoksi diperolehi di nombor gelombang 824 cm^{-1} .

Reka bentuk komposit pusat (CCD) teknik dipilih untuk menentukan keadaan optimum dalam epoksidasi TMP ester berasaskan minyak kelapa sawit. Empat pembolehubah-pembolehubah tidak bersandar telah digunakan (kepekatan CH_3COOH , kepekatan H_2O_2 , suhu, dan masa tindak balas) dengan tiga gerak balas (peratusan oksirana oksigen, nilai iodin, dan nilai hidroksil). Nilai-nilai optimum peratusan oksirana oksigen, nilai iodin, dan nilai hidroksil ialah 4.01, 1.94, dan 0.43%, masing-masing di bawah keadaan operasi berikut; 0.59 mol kepekatan asid asetik, 7.5 mol kepekatan hidrogen peroksida, suhu $50\text{ }^\circ\text{C}$ dan masa tindak balas 7 jam.

Ilmu kinetik bagi sintesis epoksidasi TMP ester berasaskan minyak kelapa sawit dikaji dalam mekanisme tertib pertama pseudo dan tertib kedua untuk pengepoksidaan kimia. Kajian kinetik dijalankan dalam dua bahagian suhu iaitu bahagian suhu rendah ($30, 50, \text{ dan } 60\text{ }^\circ\text{C}$) dan bahagian suhu tinggi ($70, 80, \text{ dan } 90\text{ }^\circ\text{C}$). Pemalar kadar untuk tertib pertama pseudo kadar model bagi suhu rendah dan tinggi dalam lingkungan $30\text{-}60\text{ }^\circ\text{C}$ dan $70\text{-}90\text{ }^\circ\text{C}$ adalah $9 \times 10^{-4} - 5.5 \times 10^{-3}$ dan $1.29 \times 10^{-2} - 2.09 \times 10^{-2}\text{ h}^{-1}$, berturut-turut. Pemalar kadar untuk tindak balas tertib kedua kadar model bagi kawasan suhu rendah dan tinggi adalah $1.3 \times 10^{-3} - 1.55 \times 10^{-2}$ dan $0.03 - 8.37 \times 10^{-2}\text{ l mol}^{-1}\text{h}^{-1}$, berturut-turut. Tenaga pengaktifan untuk tertib kedua

adalah 69.4 dan 53.3 kJmol⁻¹ untuk bahagian-bahagian suhu rendah dan suhu tinggi secara berturut-turut. Nilai-nilai tenaga pengaktifan diatas menunjukkan bahawa reaksi mudah untuk berlaku pada suhu tinggi.

Kajian kinetik kestabilan pengoksidaan juga dilakukan ke atas ep. TMP ester dan minyak komersial (minyak masak). Perbandingan kajian kinetik ep. TMP ester, dan minyak masak disiasat dengan menggunakan kalorimetri pengimbasan pembezaan (DSC) sebagai satu analisis terma. Data telah diperolehi dari DSC pada kadar pemanasan 5 °C/min. Keputusan ini menunjukkan bahawa suhu permulaan untuk pengoksidaan bagi kedua-dua minyak masak dan juga TMP ester berasaskan minyak kelapa sawit adalah pada 170°C manakala untuk ep. TMP ester berasaskan minyak kelapa sawit adalah lebih tinggi sedikit, iaitu pada 187 °C. Tenaga pengaktifan untuk pengoksidaan telah dikira menggunakan kaedah Ozawa Flynn Wall yang sesuai digunakan dalam keadaan tidak isoterma. Tenaga pengaktifan untuk ep. TMP ester, TMP ester biasa dan minyak masak masing-masing ialah 112.89, 78.28, dan 75.45 kJ/mole manakala tenaga pengaktifan dalam suhu puncak masing-masing ialah 183.1, 125.8, dan 135.5 kJ/mole. Keputusan ini membuktikan bahawa kestabilan pengoksidaan TMP ester telah diperbaiki dengan perubahan struktur ikatan berganda pada TMP ester kepada struktur cincin oksirana. Ciri-ciri pelinciran epoksidasi TMP ester berasaskan kelapa sawit juga menunjukkan potensi baik sebagai bahan asas dalam pelincir sesuai dengan peningkatan ketara dalam sifat pelinciran berbanding dengan TMP ester biasa. Walaupun nilai takat tuang lebih tinggi sedikit tetapi ciri-ciri pelinciran lain adalah lebih baik daripada ciri-ciri kebanyakan minyak-minyak komersial berasaskan minyak sayuran.

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I certify that a Thesis Examination Committee has met on **26 April 2011** to conduct the final examination of Ferra Naidir on her Doctor of Philosophy thesis entitled **“Synthesis of Oxidatively Stable Lubricant By Palm Oil-Based Epoxidized Trimethylolpropane Esters”** 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 Doctor of Philosophy.

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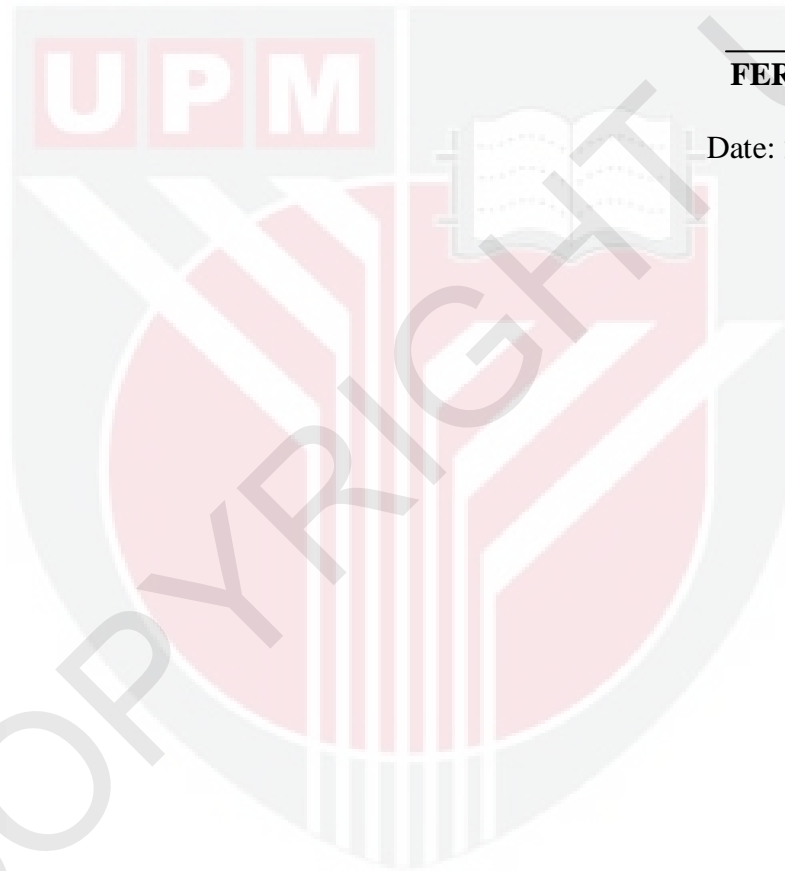
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DECLARATION

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



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Date: 26 April 2011



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