UNIVERSITI PUTRA MALAYSIA

SIMULATION OF EXTENDED REACTION KINETICS OF PALM OIL BASED POLYOL ESTERS SYNTHESIS

HAMIDAH ABD HAMID

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By

HAMIDAH ABD HAMID

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

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DEDICATED TO

MY BELOVED PARENTS

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

SIMULATION OF EXTENDED REACTION KINETICS OF PALM OIL-BASED POLYOL ESTERS SYNTHESIS

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June 2011

Chairman: Assoc. Prof. Robiah Yunus, PhD

Faculty: Engineering

The kinetics study on the synthesis of palm oil based polyol esters via transesterification between palm oil methyl esters (POME) and trimethylolpropane (TMP) has established that the reaction mechanism involves three stepwise reversible series-parallel elementary reactions. The first step of reversible monoesters esterification is suppressed by using excess POME and continual removal of methanol from the system while the other two steps are considered as reversible reactions. New kinetic modelling approach is needed in this field due to the limitation of the earlier kinetic models which had assumed complete irreversibility of all the reactions involved.

The emphasis of this work is on the simulation of complex reaction kinetics via numerical method to determine the concentration-time profiles for various species involved in the transesterification reaction between POME with TMP in a batch reactor. The attention was focused on MATLAB® simulation due to its strong

presence in the simulation field and its user-friendly factors. This research was also conducted to compare the available kinetic model via analytical solution with the new kinetic model via numerical method.

In this work, the rate equations from the previous study were extended and derived in terms of molar concentration and weight fraction-based equations. The weight fraction-based differential equations were then used as the reference for the program coding to simulate products distribution data values. In order to determine the rate constants for this kinetic model, the location of maximum local points and the final equilibrium of diesters and monoesters concentrations were considered in this study, while analyzing them statistically. The synthesis of palm oil methyl esters with trimethylolpropane was also done in a batch reactor to collect the reaction samples for certain period and then analyze them using gas chromatography system. The proposed models were verified by comparing with the data obtained from the experimental study and also with the published data available.

In general, the results from the simulation of product distributions fitted well with the experimental data. However, there was a small deviation in the experimental data which occurred at the intermediate part of the reaction due to the fluctuation in the reaction temperature. The activation energies of the reactions were between 26.3 to 28.4 kcal/mol. Statistical analysis showed that the proposed kinetic model has a good agreement with the experimental data points. The new simulation approach was found to describe experimental data values satisfactorily and the accuracy of the kinetic model had been improved and verified.

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

SIMULASI KINETIK TINDAK BALAS LANJUTAN UNTUK SINTESIS POLIOL ESTER BERASASKAN MINYAK KELAPA SAWIT

Oleh

HAMIDAH ABD HAMID

Jun 2011

Pengerusi: Prof. Madya Robiah Yunus, PhD

Fakulti: Kejuruteraan

Kajian kinetik ke atas sintesis poliol ester berasaskan minyak kelapa sawit melalui transesterifikasi antara metil ester dari minyak kelapa sawit (POME) dan trimetilolpropana (TMP) menunjukkan mekanisme tindak balas yang melibatkan tiga langkah berturutan tindak balas asas yang berbalik. Peringkat pertama iaitu tindak balas berbalik pengesteran monoester telah ditahan dengan menggunakan POME secara berlebihan dan penyingkiran metanol berterusan melalui vakum manakala dua langkah yang lain dianggap sebagai tindak balas berbalik. Pendekatan model kinetik terbaru diperlukan dalam bidang ini oleh kerana terdapat had aplikasi model-model kinetik yang telah diperkembangkan sebelum ini bagi tindak balas tersebut.

Penekanan dalam kajian ini adalah pada kinetik tindak balas kompleks melalui kaedah berangka untuk menentukan profil kepekatan-masa bagi pelbagai spesis terlibat dalam transesterifikasi antara POME dengan TMP dalam reaktor kelompok.

Tumpuan kajian telah difokuskan pada MATLAB® sesuai kekukuhan prestasinya dalam bidang simulasi dan juga mesra pengguna. Kajian ini juga telah dilakukan untuk membandingkan model kinetik yang sedia ada yang menggunakan kaedah analitik dengan model kinetik baru yang menggunakan kaedah berangka.

Dalam kajian ini, persamaan-persamaan kadar tindak balas dari kajian terdahulu telah dilanjutkan dan diterbitkan dalam bentuk kepekatan molar dan juga berasaskan pecahan berat. Persamaan pembezaan berasaskan pecahan berat kemudian telah digunakan sebagai rujukan untuk pengekodan atur cara bagi mensimulasikan taburan nilai-nilai data produk. Semua pemalar kadar ditentukan dengan mengambil kira lokasi titik maksimum dan keseimbangan ME dan DE pada akhir tindak balas, dan juga analisisa statistik. Sintesis antara POME dan TMP juga telah dilakukan dalam reaktor kelompok untuk mengumpul sampel-sampel tindak balas dan kemudian dianalisis menggunakan sistem gas kromatografi. Model yang dicadangkan telah dibuktikan bertepatan dengan data eksperimen dalam kajian ini dan juga data eksperimen yang diterbitkan sebelum ini.

Secara umum, keputusan dari simulasi bagi taburan produk adalah berpadanan dengan data eksperimen. Walaubagaimanapun, terdapat sisihan kecil pada bahagian tengah tindak balas kerana ketidakstabilan suhu tindak balas. Tenaga-tenaga pengaktifan tindak balas adalah di antara 26.3 hingga 28.4 kkal/mol. Analisis statistik menunjukkan bahawa model kinetik bertepatan dengan data eksperimen. Pendekatan simulasi baru didapati menggambarkan nilai-nilai data eksperimen yang memuaskan dan ketepatan model kinetik telah dipertingkatkan dan disahkan.

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I certify that a Thesis Examination Committee has met on 14 June 2011 to conduct the final examination of **Hamidah binti Abd Hamid** on her thesis entitled "Simulation of Extended Reaction Kinetics of Palm Oil-Based Polyol Esters Synthesis" in accordance with the Universities and University College 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 Master of Science.

Members of the Thesis Examination Committee were as follows:

Salmiaton binti Ali, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Siti Aslina binti Hussain, PhD
Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Luqman Chuah Abdullah, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Mohd Sobri Takriff, PhD
Associate Professor
Faculty of Engineering
Universiti Kebangsaan Malaysia
(External Examiner)

NORITAH OMAR, PhD
Associate Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 23 August 2011

This thesis was 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 were as follows:

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

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

HASANAH MOHD GHAZALI, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I 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, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

HAMIDAH BT ABD HAMID

Date: 14 June 2011

TABLE OF CONTENTS