UNIVERSITI PUTRA MALAYSIA

CONTINUOUS PRODUCTION OF JATROPHA CURCAS L. BIODIESEL USING OSCILLATORY FLOW BIODIESEL REACTOR

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By

AZHARI

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

May 2011

DEDICATED TO

MY PARENTS, DEAREST WIFE and DAUGHTER with love

Abstract of thesis presented to the Senate of Universiti Putra Malaysia
in fulfillment of the requirement for the degree of Doctor of Philosophy.

CONTINUOUS PRODUCTION OF *JATROPHA CURCAS* L. BIODIESEL USING OSCILLATORY FLOW BIODIESEL REACTOR

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Chair: Associate Professor Robiah Yunus, PhD

Faculty: Engineering

Jatropha curcas L. biodiesel (methyl esters) was successfully synthesized from esterified *Jatropha curcas* L. oil (JCO) via transesterification process using an oscillatory flow reactor (OFR). Alkaline catalysts were used in this process, and the effects of operating variables such as molar ratio, reaction temperature, reaction time, and the percentage of catalyst loading were investigated. The reactions were carried out under atmospheric pressure. The reaction temperatures were varied between 50 to 70 °C. The effects of two alkaline catalysts namely potassium hydroxide (KOH) and sodium hydroxide (NaOH) and molar ratio of methanol to JCO on reaction yield were investigated. The optimum conditions for batch mode in the presence of KOH catalyst were as follows: reaction temperature at 65 °C, reaction time at 30 min, molar ratio at 6:1, and catalyst amount at 1.0% w/w. The maximum reaction conversion attainable using batch process was at 99%.

The design of the OFR was carried out based on the principle of maintaining geometric and dynamic similarity of various dimensionless groups. This was followed by the application of other empirical design correlations specific to the oscillatory flow system. Using the designed OFR, the transesterification of JCO was accomplished in the presence of KOH and NaOH catalysts at the optimal conditions of 60 °C, molar ratio at 6:1, reaction time of 15 min and oscillation frequency of 6 Hz. The maximum conversion obtained was 99.7% and 90% for KOH and NaOH catalysts, respectively. The OFR performed better than the batch reactor due to its advantages in achieving a perfect superimposed mixing of fluids by forcing the upstream into the baffles area, thus a shorter time was required to complete the reaction.

One of the major problems associated with the use of biodiesel, especially prepared from palm oil, is its poor low temperature flow property. *Jatropha curcas* L. biodiesel, however, has a good low temperature property, comparable to conventional biodiesel feedstock such as rapeseed oil. This is due to the fatty acid composition of JCO which is rich in oleic and linoleic acids. From the results of analysis done on the *Jatropha curcas* L. biodiesel, the pour point and the cloud point of the biodiesel were -10 °C and -6 °C, respectively. This indicates that the oil is suitable for winter grade biodiesel. Other quality tests also showed that the *Jatropha curcas* L. biodiesel meets the majority of the quality standards of both EN 14214 and ASTM D6751.

In addition, the kinetics study on transesterification of JCO with methanol had established that the kinetics were governed by two stepwise and irreversible

elementary reactions and conformed to follow the first order reaction model. The rate constants for the formation of intermediate diglycerides and the final product *Jatropha curcas* L. methyl esters (biodiesel) were determined at various temperatures. The values of k_{TG} ranged from 0.12 to 0.17 and the values of k_{DG} ranged from 0.13 and 0.20. The activation energies for stepwise reaction in transesterification of JCO with methanol ranged from 6.55 to 11.18 kcal/mol.

Simulation of three stepwise reversible reactions in the transesterification process was also carried out using MATLAB®. The results from the simulation indicated that the reaction rate constants were affected significantly by reaction temperature. At higher temperature, the rate constant for forward reactions (k_f) increased markedly with temperature while for the reverse reactions, the rate constant (k_r) was less affected by the temperature. This is evidenced by the smaller k_r values compared to k_f values. Based on the statistical analysis, the results showed good correlations with the experimental data based on SSE, RMSE and Chi-square (χ^2) values. The proposed model for kinetics of reversible transesterification process fitted well with the experimental data.

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

PENGHASILAN BERTERUSAN BIODIESEL *JATROPHA CURCAS* L. MENGGUNAKAN REAKTOR BIODIESEL ALIRAN AYUNAN

Oleh

AZHARI

Mei 2011

Pengerusi : Profesor Madya Robiah Yunus, PhD

Fakulti : Kejuruteraan

Biodiesel *Jatropha curcas* L. (metil ester) telah berjaya disintesiskan daripada esterifikasi minyak *Jatropha curcas* L. (JCO) melalui proses pentransesteran menggunakan reaktor aliran ayunan (OFR). Antara kajian yang dijalankan termasuklah penggunaan pemangkin alkali beserta mengenalpasti kesan pembolehubah di bawah tekanan atmosfera seperti nisbah molar, suhu tindakbalas, masa tindakbalas, dan peratusan jumlah pemangkin. Suhu tindakbalas tersebut diubah antara 50 hingga 70 ^{o}C. Kesan-kesan dua pemangkin alkali dinamakan sebagai kalium hidroksida (KOH) dan natrium hidroksida (NaOH) dan nisbah molar metanol kepada JCO ke atas tindakbalas pekali telah dikaji. Keadaan yang optimum untuk mod kelompok dengan kehadiran pemangkin KOH adalah seperti berikut: suhu tindakbalas pada 65 °C, masa tindakbalas pada 30 minit, nisbah molar pada 6:1

dan jumlah pemangkin pada 1.0% w/w. Jumlah Penukaran tindakbalas maksimum yang telah dicapai menggunakan proses kelompok ialah pada 99%.

Rekaan OFR telah digunakan berdasarkan prinsip pengekalan geometri dan persamaan dinamik daripada pelbagai kumpulan tanpa dimensi. Ini diikuti dengan aplikasi spesifik korelasi rekaan empirik yang lain terhadap sistem aliran ayunan. Dengan menggunakan OFR, pentransesteran daripada JCO dilengkapkan dengan kehadiran pemangkin KOH dan NaOH pada keadaan optimal 60 °C, nisbah molar pada 6:1, masa tindakbalas pada 15 minit dan frekuensi pusingan pada 6 Hz. Penukaran maksimum diperolehi pada 99.7% dan 90% untuk pemangkin KOH dan NaOH secara berturut-turut. Melalui proses OFR, pencampuran bendalir dapat dicapai dengan sempurna melalui pemaksaan aliran atas ke dalam bahagian penampan yang menjadikan penyempurnaan tindakbalas dalam masa yang singkat dan menjadikan proses ini lebih baik dari reaktor berkelompok.

Satu daripada masalah besar yang dihadapi dengan kegunaan biodiesel terutamanya daripada minyak sawit ialah pengaliran yang sangat lemah pada suhu rendah. Walaubagaimanapun biodiesel *Jatropha curcas* L. mempunyai suhu rendah yang bagus jika dibandingkan dengan biodiesel yang kebiasaannya seperti minyak biji sawi. Ini berikutan daripada komposisi asid lemak JCO di mana ia lebih kaya dengan asid oleik dan linoleik. Daripada keputusan analisis yang telah dibuat terhadap biodiesel *Jatropha curcas* L., takat tuang dan takat awan ialah -10 °C dan -6 °C secara berturut-turut. Ini menunjukkan minyak ini sesuai untuk gred biodiesel musim sejuk. Kualiti ujian yang lain juga menunjukkan biodiesel *Jatropha curcas* L. menepati standard kualiti untuk kedua-dua EN 14214 dan ASTM D6751.

Tambahan pula, kajian kinetik ke atas pentransesteran JCO dengan metanol telah menunjukkan kinetik dikawal oleh dua peringkat sintesis dan tindakbalas asas tak berbalik yang mematuhi model tindakbalas yang pertama. Kadar pemalar kepada pembentukkan di antara diglyceride dan produk terakhir metil ester *Jatropha curcas* L. ditentukan pada suhu yang pelbagai. Nilai-nilai k_{TG} ialah julat antara 0.12 hingga 0.17 dan nilai-nilai k_{DG} ialah julat antara 0.13 hingga 0.20. Tenaga yang mengaktifan untuk tindakbalas dalam pentransesteran untuk JCO dengan metanol adalah julat antara 6.55 hingga 11.18 kcal/mol.

Simulasi tiga sintesis berperingkat tindakbalas berbalikkan dalam pentransesteran dilakukan dengan menggunakan MATLAB®. Keputusan daripada simulasi menunjukkan kadar pembolehubah tindakbalas diberi kesan daripada suhu tindakbalas. Pada suhu tindakbalas yang lebih tinggi, kadar pemalar untuk tindakbalas meningkat dengan suhu manakala tindakbalas yang berbalik, kadar pemalar memberi kesan yang kurang dengan tindakan suhu. Ini dibuktikan dengan nilai k_r dibandingkan dengan nilai k_f. Berdasarkan analisis statistik keputusan menunjukkan kolerasi yang baik dengan data ekperimen berdasarkan SSE, RMSE dan nilai Chi-square (χ^2). Model yang dicadangkan untuk proses kinetik pentransesteran berbalik, sangat sesuai dengan data eksperimen.

ACKNOWLEDGEMENTS

In the name of Allah, Most Gracious, Most Merciful

First of all, I would like to express my sincere gratitude and deep thanks to my supervisor, Assoc. Prof. Dr. Robiah Yunus for her guidance, suggestions, never-ending patience, kindness and willingness to assist me through the whole course of this research project. Without her valuable advice and support, it would not be possible for me to complete my research. I have learnt a lot of useful knowledge from her throughout this research. And also thanks to my co-supervisor, Assoc. Prof. Ir. Dr. Thomas Choong Shean Yaw and Dr. Tinia Idaty Mohd. Ghazi for their kindness assistances, supports, and suggestions so that this work could be completed properly and timely.

My high appreciation also goes to all lecturers and staff at the Department of Chemical and Environmental Engineering for their kind cooperation in providing all necessary facilities throughout the course of this study. Further gratitude also goes to my friends, especially Hamidah, Ummi, Saiful Hafiz, Ferra, Herliati, Shanti, Chong, Chang, Melina, Syuhada, Fatin, Nikman, Fatimah and Hassan for their guidance and motivation during the progress of this research.

I am also grateful to Universiti Putra Malaysia for providing financial support under Graduate Research Fellowship.

Last but not least, my biggest inspiration, my late father, Muhammad Syam, my beloved mother, Siti Khatidjah, my dearest wife, Surisna binti Umar and my daughter, Sarah Tauhida for their continuous love, support and overwhelming encouragement to finish this project thesis.

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is 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.

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AZHARI

Date: 9 May 2011

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