



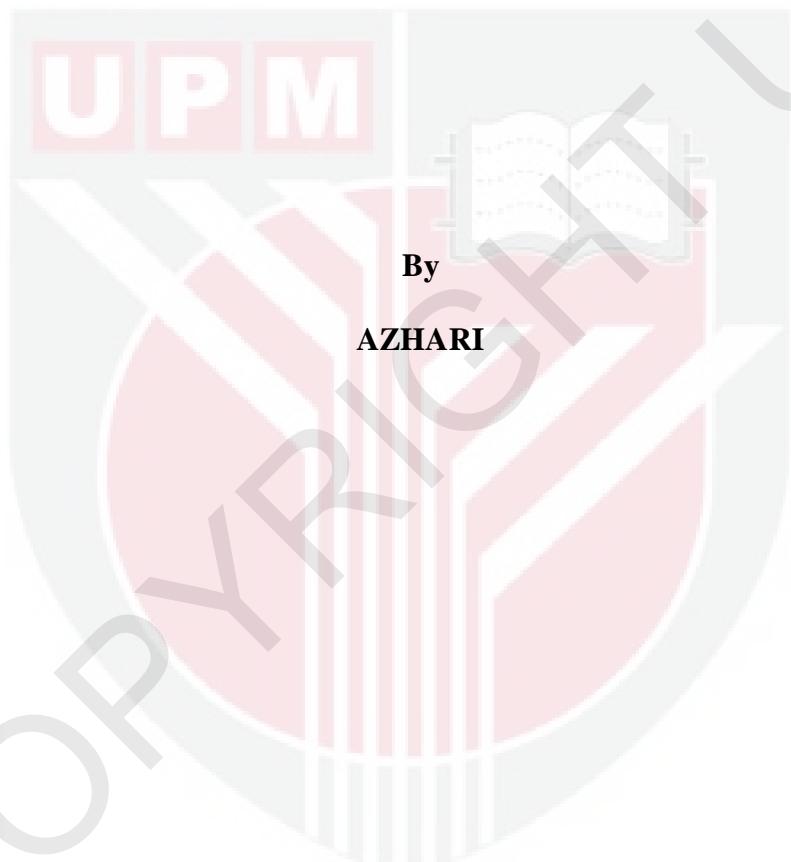
UNIVERSITI PUTRA MALAYSIA

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

AZHARI

FK 2011 80

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



**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



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**

By

AZHARI

May 2011

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 disintesikan 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 °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 penampang 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 pembentukan 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 mengaktifkan 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 eksperimen 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:

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)

Tinia Idaty Mohd. Ghazi, PhD

Lecturer

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 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.

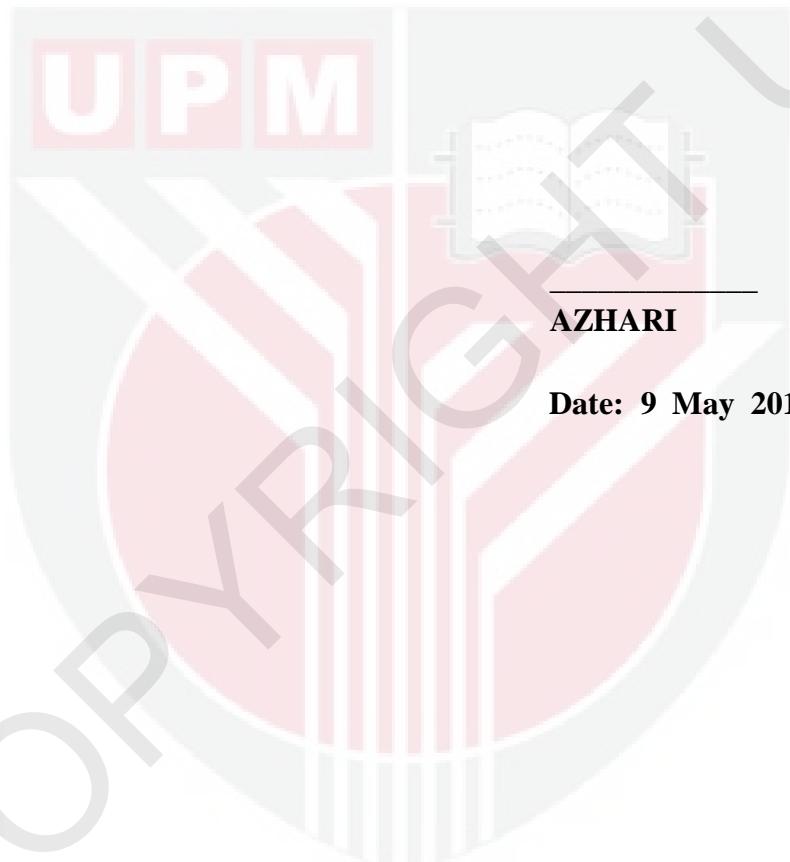


TABLE OF CONTENTS

	Page
DEDICATION	i
ABSTRACT	ii
ABSTRAK	v
ACKNOWLEDGEMENTS	viii
APPROVAL	x
DECLARATION	xii
LIST OF TABLES	xvii
LIST OF FIGURES	xix
LIST OF ABBREVIATIONS	xxii

CHAPTER

1	INTRODUCTION	1
	1.1 Background	1
	1.2 Problem Statement	5
	1.3 Objectives and Scopes of Work	9
	1.4 Thesis Outline	10
2	LITERATURE REVIEW	12
	2.1 Introduction	12
	2.2 Biodiesel	13
	2.3 Implications of Biodiesel on the Environment	16
	2.4 Blending Technique	18
	2.5 Economic Aspects	19
	2.6 Other Uses of Biodiesel	22
	2.7 <i>Jatropha curcas</i> L. Oil as Biodiesel Feedstock	23
	2.8 Waste Feedstock	27
	2.9 Continuous Process	28
	2.10 Chemical Principles	29
	2.11 Oscillatory Flow Reactor	30
	2.12 Technology of Biodiesel Production	34
	2.12.1 Esterification	34
	2.12.2 Transesterification	36
	2.12.3 Enzymatic Transesterification	40
	2.12.4 Micro emulsions	43
	2.12.5 Pyrolysis	45
	2.12.6 Supercritical Methanol	48
	2.13 Reaction Modeling and Mechanism	52
	2.14 Analysis of Reaction Products	55
	2.15 Effects of Operating Conditions	58
	2.15.1 Temperature of Reaction	58
	2.15.2 Ratio of Methanol to Oil	59
	2.15.3 Catalysts Loading	60
	2.15.4 Mixing Intensity	65
	2.15.5 Reaction Time	66

2.16	Biodiesel Quality Standards	67
2.15.1	Biodiesel Stability	71
2.15.2	Cetane Improvers	74
2.17	Low Temperature Properties	75
2.18	Summary	78
3	METHODOLOGY	81
3.1	Introduction	81
3.2	Materials and Equipment	82
3.3	Design Methods for Chemical Reactor	83
3.4	Auxiliary Equipment	86
3.5	Experimental Procedures	86
3.5.1	Pretreatment of JCO	86
3.5.2	Free Fatty Acid Analysis	87
3.5.3	Synthesis of <i>Jatropha curcas</i> L. Biodiesel Using OFR	88
3.5.4	Separation of Product	92
3.5.5	Recycle of Excess Methanol from Methyl Esters	92
3.5.6	Removal of Catalyst	92
3.6	Kinetics Study	93
3.7	Analytical Procedures	94
3.7.1	Sample Preparation for GC Injection	94
3.7.2	Gas Chromatography	94
3.8	Reduction of Water Content	95
3.8.1	Vacuum Distillation	96
3.9	Low Temperature Properties	97
3.10	Other Analytical Standard Methods	100
3.10.1	Standard Test Method for Sulfur. ASTM D 129	100
3.10.2	Standard Method for Kinematics Viscosity. ASTM D 445-09	100
3.10.3	Standard Test Method for Flash Point. ASTM D 93-02a	101
3.10.4	Standard Method for Sulfated Ash. ASTM D 874	101
3.10.5	Standard Test Method for Cetane Index. ASTM D 976-66	102
3.10.6	Standard Test Method for Distillation Recovery. ASTM D 86-10	102
3.10.7	Standard Test Method for Density. ASTM D 4052-09	103
3.10.8	Standard Methods for Carbon Residue on 10%. ASTM D 189-76	103
3.10.9	Standard Test Method for Cloud Point. ASTM D 2500 – 66	104
3.10.10	Standard Test Method for Water by Distillation. ASTM D 95-99	104
3.10.11	Standard Test Method for Copper Corrosion. ASTM D 130	104
3.10.12	Standard Test Method for Carbon and Hydrogen. ASTM 777-08	105

3.10.13	Standard Test Method for Phosphorous. ASTM 4591-09	105
3.10.14	Standard Test Method for Total Acid Number. ASTM 974-08e1	106
3.10.15	Standard Test Method for Oxidation Stability. ASTM D 943-04a	107
3.10.16	Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter. ASTM D240	107
3.10.17	Standard Test Method for Saponification Number of Petroleum Products. ASTM D94	108
3.11	Modeling of the Reaction Kinetics	108
3.12	Safety Precaution	109
4	DESIGN OF OSCILLATORY FLOW REACTOR SYSTEM	
4.1	Introduction	111
4.2	Mass and Energy Balance	113
4.2.1	Mass Balance	114
4.2.2	Energy Balance	116
4.3	Mechanical Design	120
4.3.1	Corrosion Allowance	121
4.3.2	Design of Baffle and Tube	121
4.3.3	Design of the Heating Jacket	126
4.3.4	Design of Chemical Tank	127
4.3.5	Pump Specification	128
4.4	Materials of Construction	130
4.5	Control and Instrumentation	130
5	PRETREATMENT OF BIODIESEL FEEDSTOCK	132
5.1	Introduction	132
5.2	Free Fatty Acid Content in JCO	135
5.3	Decreasing of FFA Content	137
5.3.1	Effect of Reaction Temperature	138
5.3.2	Effect of Sulfuric Acid Concentration	139
5.3.3	Effect of Methanol to JCO Ratio	141
5.3.4	Effect of Reaction Time	142
5.4	Effect of FFA Content on Transesterification	144
5.5	Conclusion	145
6	BIODIESEL PRODUCTION VIA TRANSESTERIFICATION	146
6.1	Introduction	146
6.2	Transesterification in Stirred Batch Reactor	147
6.2.1	Effect of Methanol to JCO Molar Ratio	148
6.2.2	Effect of Reaction Temperature	149
6.2.3	Effect of Reaction Time	150
6.2.4	Effect of Catalyst Loading	152
6.3	Transesterification in OFR	154
6.3.1	Effect of Oscillation Frequency	154

6.3.2	Effect of Reactants Molar Ratio	157
6.3.3	Effect of Residence Time	158
6.3.4	Effect of Catalyst and Reaction Temperature	160
6.4	Conclusion	162
7	KINETICS OF REACTION AND MODELING	165
7.1	Introduction	165
7.2	Reaction Kinetics	167
7.3	Determination of Reaction Rate Constant	171
7.4	Determination of Activation Energy	177
7.5	Modeling of Reversible Reaction	179
7.5.1	Derivation of Mathematical Model	181
7.5.2	Model of Reversible Transesterification Reaction	183
7.6	Statistical Analysis of the Kinetics Model	189
7.7	Conclusion	191
8	BIODIESEL PROPERTIES TESTING	193
8.1	Introduction	193
8.2	Physical Properties of Biodiesel	195
8.2.1	Density	196
8.2.2	Kinematic Viscosity	196
8.2.3	Pour Point	197
8.2.4	Cloud Point	199
8.2.5	Water Content	200
8.2.6	Total Acid Number	200
8.2.7	Saponification Number	201
8.2.8	Iodine Value	203
8.2.9	Calorific Value	203
8.2.10	Flash Point	204
8.2.11	Sulphated Ash	205
8.2.12	Carbon Residue	206
8.2.13	Cetane Index	207
8.2.14	Copper Strip Corrosion	207
8.2.15	Distillation Temperature	208
8.2.16	Phosphorous	209
8.2.17	Oxidative Stability	209
8.2.18	Carbon and Hydrogen	211
8.3	Conclusion	212
9	CONCLUSION AND RECOMMENDATIONS	214
9.1	Conclusion	214
9.2	Recommendations	217
REFERENCES		219
APPENDICES		239
BIODATA OF STUDENT		272
LIST OF PUBLICATIONS		273