

**BIODIESEL PRODUCTION USING
HETEROGENEOUS CATALYST
AND DEVELOPMENT OF QUALITY
FAST CHECK TEST KIT**

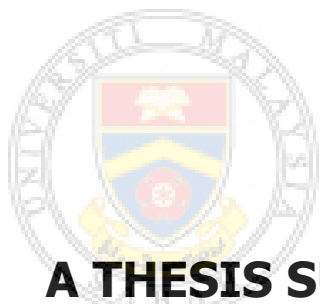


KAY KIAN HEE

UMS
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**SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITI MALAYSIA SABAH
2015**

**BIODIESEL PRODUCTION USING
HETEROGENEOUS CATALYST
AND DEVELOPMENT OF QUALITY
FAST CHECK TEST KIT**



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UMS

**A THESIS SUBMITTED IN FULFILLMENT
WITH THE REQUIREMENT FOR THE DEGREE
DOCTOR OF PHILOSOPHY**

**SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITI MALAYSIA SABAH
2015**

DECLARATION

I hereby declare that the materials in this thesis are original except for quotations, summaries and references, each of which have been duly acknowledged.

16th March 2015

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Kay Kian Hee
PS2010 – 8221



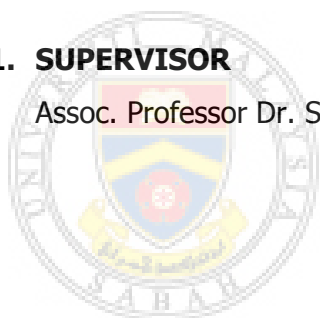
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CERTIFICATION

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MATRIC NO. : **PS2010 – 8221**
TITLE : **BIODIESEL PRODUCTION USING HETEROGENEOUS
CATALYST AND DEVELOPMENT OF QUALITY FAST
CHECK TEST KIT**
DEGREE : **DOCTOR OF PHILOSOPHY (INDUSTRIAL CHEMISTRY)**
VIVA DATE : **11 SEPTEMBER 2014**

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ACKNOWLEDGEMENT

First of all, I would like to acknowledge the financial and technical support from Yanmar Kota Kinabalu R&D Center Sdn Bhd (YKRC), which had made this study possible and helping me to complete my research project.

In addition, I would like to acknowledge my supervisor, Associate Professor Dr. Suhaimi Yasir, for his dedicated guidance, helpful ideas, suggestions, and discussions that contribute to the remarkable success achieved in this work.

My deepest appreciation is extended to all YKRC Staff, particularly to YKRC Managing Director, Mr. Takashi Saeki, Finance and Administration Manager, Ms. Christine Chiew Nguat Poh, Fuel R&D group member, Ms. Beverly Kah, Ms. Michelle Ni Fong Fong, Mr. Kamaruddin Kudumpor, for their kind and valuable assistance while doing my research works in this years. My appreciation also to all staff who have involved directly and indirectly throughout this research project.

I would like also to express my special thanks to, particularly to Mr. Hiroshi Kanda, Mr. Makoto Yuri, Mr. Genshi Yasuma, Mr. Yuki Otomo, Mr. Ch'ng Ee Hong for their guidance, encouragement, motivation, and expectations are indispensable to my achievements and will serve as a continuous inspiration for my research.

Last but not least, my deepest gratitude to my wife, Cynthia Lim Fui Foo, my daughter, Ivory Kay Tse Xing and Kay's family for their undying and unconditional love, supports and encouragements.

KAY KIAN HEE

13th March 2015

ABSTRACT

Biodiesel is receiving increasing attention as an alternative, non-toxic, biodegradable, and renewable diesel fuel. The cost of feedstock in the form of neat vegetable oils is significantly 70-95% of the total cost of the biodiesel production. Low quality oil is potential low cost feedstock to be used in biodiesel production. However, it contains high concentrations of free fatty acids (FFA) and water contain. The conventional technology is not suitable to adopt basic homogeneous catalyst due to saponification between basic catalyst and the FFA. In order to efficiently utilize these low cost feedstocks for biodiesel synthesis, development a new class of high efficiency heterogeneous catalysts, which has, high FFA and water-tolerance that could show promising performances of transesterification is necessary. FFA and water adsorption characteristics of both zeolites were investigated according to batch method under varying conditions, namely different shaking time, initial concentration and solid – solution ratio. The concentration of FFA (as Total Acid Number) and water in all samples was determined according to the EN14104 and EN14101 standard method respectively. Percent FFA and water adsorption by both natural zeolite and NaOCH₃-Zeolite increases with shaking time (attaining equilibrium after 60 min) and solid – solution ratio. The FFA adsorption conforms strongly to pseudo – 2nd order kinetics ($R^2 = 0.9894$ and $R^2 = 0.9989$) and Freundlich ($R^2 = 0.9972$ and $R^2 = 0.9979$) whereas the water adsorption by both zeolites conforms strongly to pseudo – 2nd order kinetics ($R^2 = 0.9801$ and $R^2 = 0.9740$) and Langmuir isotherm ($R^2 = 0.9953$ and $R^2 = 0.9957$). For the biodiesel transesterification, the effects of various factors consist of the reaction time, molar ratio of methanol to oil, reaction temperature, mass ratio of catalyst to oil and catalyst reusability were investigated. The experimental treatments of a 20:1 molar ratio of methanol to oil, addition of 5wt% NaOCH₃-zeolite catalyst, 70°C reaction temperature and 5 cycles reusability using low quality crude jatropha oil resulted in optimum yield in which the biodiesel content reached 97.4wt% at 6 h without soap formation. This biodiesel was characterized for its physical and chemical properties as ASTM or EN-compliant biodiesel. Performance (BSFC, BTE and EGT) and emission characteristics (smoke density) of this biodiesel with diesel fuel were examined and compared in a direct injection (DI) diesel engine. Brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE) for biodiesel was higher than diesel fuel with 13.12% and 0.41% for mean value, respectively. A comparison of exhaust emissions showed that smoke density of biodiesel is lower than those of diesel fuel by 44.4%. Fast check analysis method with special measuring device and chemical solvent mixture were developed to provide on-site analysis check for biodiesel quality monitoring. Biodiesel Test Kit have shown comparable result with ASTM D7371 with correlation coefficient ($R^2 > 0.99$) for biodiesel-diesel blends B5, B10 and B20 of Palm, Jatropha and Soybean based biodiesel. Triglycerides Test Kit have shown good correlation coefficient ($R^2 > 0.99$) for triglycerides 3, 4 and 5%(v/v). The developed methods are providing fast, simple and affordable on-site fast check analysis in measuring FAME content in diesel & triglycerides content in final FAME product economically especially in rural area.

ABSTRAK

PENGHASILAN BIODIESEL MENGGUNAKAN MANGKIN HETEROGEN DAN PEMBANGUNAN KIT ANALYSIS KUALITI

Biodiesel mendapat sambutan hangat sebagai bahan bakar alternatif yang tidak bertoksik, boleh terbiodegradasi serta boleh dikitar semula. Minyak berkualiti rendah yang juga merupakan bahan mentah berkost rendah berpotensi untuk digunakan dalam penghasilan biodiesel. Walau bagaimanapun, ia mengandungi kepekatan asid lemak bebas (FFA) dan kandungan air yang tinggi. Ini menyebabkan ia tidak sesuai digunakan dalam teknologi lama untuk penghasilan biodiesel iaitu menggunakan mangkin homogen berkali yang boleh menyebabkan proses penyabunan antara mangkin alkali dengan FFA. Untuk mengoptimalkan penggunaan bahan mentah yang berkost rendah, penghasilan kelas mangkin berprestasi tinggi yang dapat mengatasi kandungan FFA dan air yang tinggi perlu dilakukan. Sifat penyerapan FFA dan air pada zeolit masing-masing dikaji berdasarkan kaedah berkumpulan menggunakan keadaan seperti tempoh pengacauan berbeza, kepekatan awal dan nisbah pepejal-cecair. Kepekatan FFA (dalam bentuk jumlah nombor keasidan) dan air dalam semua sampel ditentukan berdasarkan kaedah piawai EN14104 dan EN14101. Kadar peratus penyerapan FFA dan air meningkat dengan tempoh pengacauan (mencapai keseimbangan selepas 60 minit) dan pengacauan mengikut nisbah pepejal-cecair tertentu. Penyerapan FFA dibuktikan melalui pseudo-kinetik tertib kedua ($R^2 = 0.9894$ dan $R^2 = 0.9989$) dan Freundlich ($R^2 = 0.9972$ dan $R^2 = 0.9979$) manakala penyerapan air oleh kedua-dua zeolit dibuktikan melalui pseudo-kinetik tertib kedua ($R^2 = 0.9801$ dan $R^2 = 0.9740$) dan isoterma Langmuir ($R^2 = 0.9953$ dan $R^2 = 0.9957$). Bagi transesterifikasi biodiesel, faktor yang dikaji adalah tempoh tindak balas, nisbah molar metanol dengan minyak, suhu tindak balas, nisbah berat mangkin dengan minyak dan kebolegunaan semula mangkin. Eksperimen untuk nisbah 20:1 metanol kepada minyak, 5wt% mangkin NaOCH_3 -zeolite, suhu tindak balas 70°C dan 5 kitaran kebolegunaan semula menggunakan minyak jarak pagar mentah menghasilkan biodiesel dengan hasil optimum mencapai 97.4wt% dalam tempoh 6 jam tanpa berlakunya pembentukan sabun. Pencirian fiziko kimia biodiesel ini mematuhi ciri biodiesel dalam ASTM atau EN. Prestasi (BSFC, BTE dan EGT) dan ciri emisi (ketumpatan asap) biodiesel ini dengan diesel dikaji dan dibandingkan menggunakan enjin diesel suntikan langsung (DI). Brek spesifik penggunaan bahan bakar (BSFC) dan brek kecekapan haba (BTE) untuk biodiesel adalah lebih tinggi daripada diesel dengan masing-masing nilai min 13.12% dan 0.41%. Perbandingan pelepasan ekzos menunjukkan ketumpatan asap biodiesel yang lebih rendah daripada diesel sehingga 44.4%. Kaedah analisis pemeriksaan pantas dengan menggunakan alat khas dan campuran bahan kimia dibangunkan untuk memberi pemeriksaan analisis in-situ untuk pemantauan kualiti biodiesel. Kit analisis menunjukkan hasil setaraf dengan ASTM D7371 dengan korelasi pekali ($R^2 > 0.99$) untuk campuran biodiesel-diesel B5, B10 dan B20 bagi biodiesel berasaskan sawit, jarak pagar dan kacang soya. Kit pemeriksaan trigliserida menunjukkan korelasi pekali yang baik ($R_2 > 0.99$) trigliserida 3, 4 and 5%(v/v).

TABLE OF CONTENTS

	Pages
TITLE PAGE	i
DECLARATION	ii
CERTIFICATION	iii
ACKNOWLEDGEMENT	iv
ABSTRACT	v
<i>ABSTRAK</i>	vi
TABLE OF CONTENTS	vii
LIST OF TABLES	xi
LIST OF FIGURES	xiv
LIST OF ABBREVIATIONS AND SYMBOLS	xviii
CHAPTER 1: INTRODUCTION	
1.1 Biodiesel	1
1.2 Conventional Methods for Biodiesel Production	2
1.3 Current Standard Methods for Biodiesel Quality Monitoring	2
1.4 Problems Encounter in the Biodiesel Production	3
1.5 Hypothesis	3
1.6 Objectives	4
1.7 Scope of Study	4
CHAPTER 2: LITERATURE REVIEW	
2.1 Introduction of Biodiesel	5
2.2 Benefit of Biodiesel	6
2.3 Biodiesel Feedstock	8
2.4 Biodiesel Production	10
2.5 Mechanism of Catalysts in Biodiesel Production	16
2.6 High Free Fatty Acid (FFA) and water content in Oil	17
2.7 Heterogeneous Catalysts in Biodiesel Production	19
2.8 Zeolite	20

2.9	Application of Zeolite as Catalysts in Biodiesel Production	21
2.10	Basic theory of adsorption	22
2.11	Characteristics of adsorption	24
2.12	Adsorption kinetics	26
2.13	FFA and Water adsorption by Zeolite	27
2.14	Application of Biodiesel in Diesel Engine	31
2.15	Biodiesel Quality Specification	34
2.16	Blended Biodiesel Quality Monitoring	37
2.17	Biodiesel Purity Monitoring	38
2.18	Fast Check Analysis	41

CHAPTER 3: MATERIALS AND METHODS

3.1	Research Materials	42
3.2	Methodology	42
3.2.1	Catalyst Preparation	42
3.2.2	Sample Preparation	43
3.2.3	Adsorption of FFA and Water on Zeolite	43
3.2.4	Catalyst Characterization	46
3.2.5	Transesterification	47
3.2.6	Diesel Engine Performance Test	51
3.2.7	Fuel Blending	53
3.2.8	Solubility Test	54
3.2.9	Biodiesel Test Kit	54
3.2.10	Triglycerides Test Kit	56
3.3	Sample Analysis	57
3.3.1	Determination of Density	57
3.3.2	Determination of Kinematic Viscosity	58
3.3.3	Determination of Flash Point	58
3.3.4	Determination of Carbon Residue	58
3.3.5	Determination of Water Content	59
3.3.6	Determination of Oxidation Stability	59
3.3.7	Determination of Total Acid Number	60
3.3.8	Determination of Iodine Value	60

3.3.9	Determination of Ester Content & Linolenic acid	61
3.3.10	Determination of Free-, Total-, Mono-, Di- & Triglyceride Content	62
3.3.11	Determination of Methanol Content	63
3.3.12	Determination of Sodium, Potassium, Calcium and Magnesium	64
3.3.13	Determination of Phosphorus	65
3.3.14	Determination of Calorific value	65
3.3.15	Determination of Biodiesel blending percentage	65

CHAPTER 4: REMOVAL OF FREE FATTY ACID AND WATER CONTENT FROM LOW QUALITY OIL BY ZEOLITE

4.1	Quality of the Crude Jatropha Oil	67
4.2	Removal of Free Fatty Acid (FFA) and Water Adsorption	70
4.2.1	Effect of shaking time	70
4.2.2	Adsorption isotherms for FFA and water adsorption	79
4.2.3	Effect of solid – solution ratio	83
4.2.4	Comparison between natural zeolite and NaOCH ₃ -zeolite	85
4.3	Summary	85

CHAPTER 5: BIODIESEL PRODUCTION FROM LOW QUALITY CRUDE JATROPHA OIL USING HETEROGENEOUS CATALYST

5.1	Catalyst Characterization	87
5.2	Oil Characterization	94
5.3	Effect of ion exchange on zeolite	96
5.4	Effect of Reaction Time	97
5.5	Effect of Temperature	99
5.6	Effect of Methanol – Oil Molar Ratio	100
5.7	Effect of Catalyst Dosage	101
5.8	Effect of Particle Size	103
5.9	Reusability Test	104
5.10	Room Temperature Biodiesel Production	105
5.11	Brake Specific Fuel Consumption (BSFC)	106

5.12	Exhaust Temperature	107
5.13	Smoke Density	109
5.14	Summary	109

CHAPTER 6: DEVELOPMENT OF FAST CHECK TEST KIT FOR OIL QUALITY MONITORING

6.1	Fuel Characterization	112
6.2	Fuel Blending	112
6.3	Solubility Test	116
6.4	Measurement of Biodiesel Content using Biodiesel Test Kit	117
6.5	Triglycerides Test Kit	120
6.6	Summary	122

CHAPTER 7: CONCLUSIONS

7.1	Removal of Free Fatty Acid and Water Content from Low Quality Oil by Zeolite	123
7.2	Biodiesel Production From Low Quality Crude Jatropha Oil using Heterogeneous catalyst	124
7.3	Engine Performance Characteristics of Jatropha Biodiesel transesterified from Low Quality Crude Jatropha Oil	124
7.4	Development of Fast Check Test Kit For Oil Quality Monitoring	125
7.5	Implications of the research finding	125
7.6	Recommendations for future work	125

REFERENCES	127
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LIST OF TABLES

	Page
Table 2.1: Classification of biodiesel generation based on the merits and demerits	9
Table 2.2: Typical fatty acid composition-common oil source	10
Table 2.3: Comparison of homogeneous and heterogeneously catalyzed transesterification	13
Table 2.4: Merits and demerits of alkaline and acidic heterogeneous Catalysts	15
Table 2.5: Transesterification using zeolites of previous studies	23
Table 2.6: Representative formula and selected physical properties of important zeolites.	28
Table 2.7: Acid removal using zeolites of previous studies	30
Table 2.8: Water Adsorption using zeolites of previous studies	31
Table 2.9: Comparison of the standards for diesel and biodiesel based on European Standard (EN) and American Society for Testing and Materials (ASTM)	36
Table 3.1: Test conditions for the FFA adsorption studies	44
Table 3.2: Test conditions for the water adsorption studies	45
Table 3.3: Conditions for the transesterification studies	48
Table 3.4: Diesel Engine Specifications	52
Table 3.5: Conditions for the solubility test	54
Table 4.1: Characterization of Crude Jatropha Oil and Jatropha Biodiesel	68
Table 4.2: Fatty acid composition of Jatropha Biodiesel	69
Table 4.3: Values of pseudo first order, pseudo second order and intra particle diffusion parameters for FFA adsorption by natural zeolite and NaOCH ₃ -zeolite	77
Table 4.4: Values of pseudo first order, pseudo second order and intra particle diffusion parameters for water adsorption by natural zeolite and NaOCH ₃ -zeolite	77

Table 4.5:	Values of Langmuir and Freundlich isotherms parameters for FFA adsorption in zeolite	81
Table 4.6:	Values of Langmuir and Freundlich isotherms parameters for water adsorption in zeolite	82
Table 4.7:	Separation factor (RL) values for FFA adsorption by zeolite	82
Table 4.8:	Separation factor (RL) values for water adsorption by zeolite	83
Table 5.1:	Chemical Composition of natural zeolite and modified zeolite using EDS analysis	87
Table 5.2:	Physicochemical properties of the zeolite catalysts	90
Table 5.3:	Basic strength and basicity of natural zeolite and modified zeolite	92
Table 5.4:	Charaterization of Crude Jatropha Oil and Jatropha Methyl Ester	95
Table 5.5:	Examples of studies on transesterification reaction time using zeolite as catalyst	98
Table 5.6:	Examples of studies on transesterification temperature using zeolite as catalyst	100
Table 5.7:	Examples of studies on transesterification Methanol – Oil Molar Ratio using zeolite as catalyst	101
Table 5.8:	Examples of studies on transesterification catalyst dosage using zeolite as catalyst	103
Table 6.1:	Charaterization of Jatropha Biodiesel and Diesel Fuel	113
Table 6.2:	Analysis accuracy of biodiesel blending percentage (B5, B10 and B20) of various feedstock biodiesel (Palm, Jatropha and Soybean) mixture with diesel based on ASTM D7371 analysis at wave number 1740cm ⁻¹	115
Table 6.3:	Analysis accuracy of triglycerides content of various feedstock biodiesel mixture with plant oil based on EN 14105 analysis	116
Table 6.4:	Solubility of diesel, biodiesel and triglycerides in various alcohols	117
Table 6.5:	Result Summary of Biodiesel Test Kit	118
Table 6.6:	Analysis precision and detection limit of Biodiesel Fast Check Test Kit	119

Table 6.7:	Comparison of Actual Fuel Sample Analysis Result of FTIR and Biodiesel Test Kit	119
Table 6.8:	Result Summary of Triglyceride Test Kit	121
Table 6.9:	Analysis precision and detection limit of Triglycerides Fast Check Test Kit	121
Table 6.10:	Comparison of Actual Fuel Sample Analysis Result of GC and Triglycerides Test Kit	121



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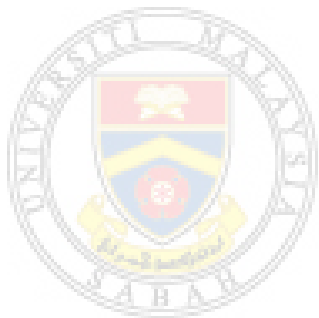
LIST OF FIGURES

	Page
Figure 2.1: Transesterification reaction of triglycerides	11
Figure 2.2: The transesterification reactions of vegetable oil with alcohol to esters and glycerol	12
Figure 2.3: (a) Base catalyst reaction with FFAs to produce soap and water, both undesirable byproducts. (b) Water promotes the formation of FFAs.	14
Figure 2.4: Homogeneous base catalyzed mechanism for transesterification	16
Figure 2.5: Homogeneous acid catalyzed mechanism for transesterification	17
Figure 2.6: Saponification of soap formation between FFA and base catalyst	18
Figure 3.1: Catalyst preparation using impregnation method	43
Figure 3.2: Transesterification method	47
Figure 3.3: Yanmar NFD direct-injected (DI) diesel engine	52
Figure 3.4: Blended Biodiesel with diesel preparation	53
Figure 3.5: Blended Biodiesel with plant oil preparation	53
Figure 3.6: Prototype of Biodiesel Test Kit	55
Figure 3.7: Diagram illustrated states before and after the measuring method for measuring the FAME % in diesel according to the embodiment of the present invention	55
Figure 3.8: Prototype of Triglyceride Test Kit	56
Figure 3.9: Diagram illustrated states before and after the measuring method for measuring the triglycerides in biodiesel according to the embodiment of the present invention	57
Figure 4.1: Gas Chromatograms of Ester Content and Fatty Acid Composition in Jatropha Biodiesel	70
Figure 4.2: Percentage FFA adsorbed by natural zeolite versus shaking time at different solid – solution ratios	71
Figure 4.3: Percentage FFA adsorbed by NaOCH ₃ -zeolite versus shaking time at different solid – solution ratios	71

Figure 4.4:	Percentage water adsorbed by natural zeolite versus shaking time at different solid – solution ratios	72
Figure 4.5:	Percentage water adsorbed by NaOCH ₃ -zeolite versus shaking time at different solid – solution ratios	72
Figure 4.6:	Pseudo first – order kinetic plot for the adsorption of FFA by natural zeolite and NaOCH ₃ -zeolite	74
Figure 4.7:	Pseudo first – order kinetic plot for the adsorption of water by natural zeolite and NaOCH ₃ -zeolite	74
Figure 4.8:	Pseudo second – order kinetic plot for the adsorption of FFA by natural zeolite and NaOCH ₃ -zeolite	75
Figure 4.9:	Pseudo second – order kinetic plot for the adsorption of water by natural zeolite and NaOCH ₃ -zeolite	75
Figure 4.10:	Intra particle diffusion kinetic plot for the adsorption of FFA by (a) natural zeolite and (b) NaOCH ₃ -zeolite	76
Figure 4.11:	Intra particle diffusion kinetic plot for the adsorption of water by (a) natural zeolite and (b) NaOCH ₃ -zeolite	76
Figure 4.12:	Rate constant versus solid – solution ratio for the adsorption of FFA by Zeolite	78
Figure 4.13:	Rate constant versus solid – solution ratio for the adsorption of water by Zeolite	78
Figure 4.14:	Freundlich isotherm for FFA adsorption by Natural Zeolite and NaOCH ₃ -Zeolite	79
Figure 4.15:	Freundlich isotherm for water adsorption by Natural Zeolite and NaOCH ₃ -Zeolite	80
Figure 4.16:	Langmuir isotherm for FFA adsorption by Natural Zeolite and NaOCH ₃ -Zeolite	80
Figure 4.17:	Langmuir isotherm for water adsorption by Natural Zeolite and NaOCH ₃ -Zeolite	81
Figure 4.18:	FFA adsorption by zeolite at different solid – solution ratios	84
Figure 4.19:	Water adsorption by zeolite at different solid – solution ratios	84
Figure 5.1:	XRD patterns for sample (a) Natural Zeolite, (b) NaOCH ₃ -Zeolite, (c) NaOH-Zeolite and (d) KOH-Zeolite	89
Figure 5.2:	N ₂ isotherms of the natural zeolite and modified zeolite	91

Figure 5.3:	Scanning electron microscopy image of (a) Natural Zeolite, (b) NaOCH ₃ -Zeolite, (c) NaOH-Zeolite and (d) KOH-Zeolite	93
Figure 5.4:	Effect of various modified zeolite on ester content in transesterification	96
Figure 5.5:	Effect of reaction time on ester content in transesterification	98
Figure 5.6:	Effect of reaction temperature on ester content in transesterification	99
Figure 5.7:	Effect of methanol to oil molar ratio on ester content in transesterification	101
Figure 5.8:	Effect of catalyst dosage on ester content in transesterification	102
Figure 5.9:	Effect of catalyst particle size on ester content in transesterification	103
Figure 5.10:	Effect of catalyst reusability on ester content in transesterification	105
Figure 5.11:	Effect of room temperature on ester content in transesterification	106
Figure 5.12:	Brake Specific Fuel Consumption (BSFC) versus brake mean effective pressure	107
Figure 5.13:	Exhaust temperature with brake mean effective pressure	108
Figure 5.14:	Smoke density with brake mean effective pressure	109
Figure 6.1:	FTIR peak of biodiesel blending percentage (B0, B5, B10, B20 & B100) of various feedstock biodiesel (Palm, Jatropha and Soybean) mixture with diesel based on ASTM D7371 analysis at wave number 1740cm ⁻¹	114
Figure 6.2:	Biodiesel blending percentage (B5, B10 and B20) of various feedstock biodiesel (Palm, Jatropha and Soybean) mixture with diesel based on ASTM D7371 analysis at wave number 1740cm ⁻¹	114

Figure 6.3:	Gas Chromatograms of Triglycerides (TG3, TG 4 and TG 5) blending percentage of various feedstock biodiesel (Palm, Jatropha and Soybean) mixture with plant oil based on EN14105 analysis	115
Figure 6.4:	Triglycerides (TG) blending percentage of various feedstock (Palm, Jatropha and Soybean) biodiesel mixture with plant oil based on EN14105 analysis	116
Figure 6.5:	Result of Biodiesel Test Kit using various feedstock (Palm, Jatropha and Soybean) blended biodiesel	118
Figure 6.6:	Result Triglyceride Test Kit using various feedstock biodiesel	120



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ABBREVIATIONS AND SYMBOLS

~	-	about
±	-	plus/minus
⇌	-	equilibrium
[]	-	concentration
ASTM	-	American Society for Testing and Materials
B5	-	5vol% biodiesel blending with diesel
CJO	-	Crude Jatropha Oil
cm³	-	cubic centimeter
EN	-	European Standard
FAME	-	Fatty Acid Methyl Ester
FFA	-	free fatty acid
FTIR	-	Fourier transform infrared spectroscopy
g	-	gram
J/g	-	joule per gram
mg KOH/g	-	milligram Potassium Hydroxide per gram
mg/L	-	milligram per liter
NaOCH₃	-	Sodium methoxide
NaOCH₃-Zeolite	-	Sodium methoxide Zeolite
NaOH-Zeolite	-	Sodium hydroxide Zeolite
R²	-	Correlation Coefficient
rpm	-	rotation per minute
s	-	second
µm	-	micrometer
Vol%	-	volume percentage
wt%	-	weight percentage

CHAPTER 1

INTRODUCTION

1.1 Biodiesel

Biodiesel is receiving increasing attention as an alternative, renewable, non-toxic, biodegradable, carbon neutral and environmentally benign fuel for diesel engines has been attracting considerable interest all over the world which can significantly reduce global warming and the dependence on conventional fossil fuels (Atabani *et al.*, 2013; Yahyaee *et al.*, 2013). Biodiesel is a mono alkyl ester of fatty acids obtained by transesterification of the triglycerides contained in vegetable oils and animals fats which involves alcohol and vegetable oil in the presence of a catalyst to yield biodiesel and glycerol (Chattopadhyay *et al.*, 2011; Salamanca *et al.*, 2012; Pinzi *et al.*, 2013). The triglyceride used for biodiesel production could be vegetable oils such as soybean, canola, palm and sunflower oils or animal fats such as, beef tallow and even waste cooking oils and algae oil (Corro *et al.*, 2013; Lapuerta *et al.*, 2013; Liu *et al.*, 2013; Man *et al.*, 2013; Zhao *et al.*, 2013).

Biodiesel offers some technical advantages as compared to conventional petroleum diesel such as biodegradability, higher flash point, higher cetane number, reduced exhaust emissions (Kannan *et al.*, 2012; Fazal *et al.*, 2013). Biodiesel can be used as fuel for diesel engines, either pure or mixed with petroleum distillates to attain blends defined with the abbreviation BX, where B stands for biodiesel and X stands for the biodiesel percentage (volume/volume) (Fernando *et al.*, 2007; Bunce *et al.*, 2010). In order to give a quality assurance to the users, the biodiesel produced must meet the specification of ASTM D6751 and EN 14214 so that it can be used directly to run the existing diesel engines without major modifications or as a biodiesel blended with petrol diesel to create less hazardous emissions (Oliveira *et al.*, 2006; Hoekman *et al.*, 2012). European Standard EN 14214 specifies a minimum percentage of 96.5 wt% ester content in biodiesel purity which is significantly influence the performance of diesel engines. The limits for physical and chemical

properties specified in these standards guarantee the safe use of biodiesel in internal combustion engines when used in the pure form or when mixed with conventional diesel at different percentages (Ciubota-Rosie *et al.*, 2013).

1.2 Conventional Methods for Biodiesel Production

Various conventional methods have been used for biodiesel production through transesterification from various types of oil feedstock. Transesterification can be catalyzed by both acidic-catalysts (e.g. HCl and H₂SO₄) and basic-catalysts (e.g. KOH and NaOH) (Ma & Hana, 1999). Alkaline catalysts are widely investigated because the rate of transesterification reaction by alkaline catalysts is much faster than that by acid catalysts (Marchetti *et al.*, 2007). Currently many heterogeneous catalysts have been used in the transesterification process to produce biodiesel at lower cost and environmentally friendly. Heterogeneous transesterification method is more superior compared to the homogenous transesterification method especially on the separation and purification of the product (FAME) (Demirbas, 2007; Zabeti, 2009).

1.3 Current Standard Methods for Biodiesel Quality Monitoring

Many analytical techniques have been developed for the quantification of biodiesel content in the biodiesel-diesel blend (Knothe, 2006; Pimentel *et al.*, 2006). Methods based on Fourier transform mid-infrared (FT-IR) absorption spectroscopy (Santos *et al.*, 2005; Aliske *et al.*, 2007; Lira *et al.*, 2010), liquid and gas chromatography (Nicola *et al.*, 2008; Ragonese *et al.*, 2009), nuclear magnetic resonance spectroscopy (Knothe, 2006; Monteiro *et al.*, 2009;), ultraviolet absorption spectroscopy (Zawadzki *et al.*, 2007), near infrared spectroscopy (Oliveira *et al.*, 2006; Pimentel *et al.*, 2006; Fernandes *et al.*, 2011) have been reported.

For biodiesel purity assessment, international standard methods, such as EN14105 and ASTM 6584, among others are used to do the quality control of biodiesel which use gas chromatography technique. Results from these analyses can give information about whether or not the sample is adulterated with unreacted raw vegetable oils which will lead to injector fouling and may also contribute to the formation of deposits at injection nozzles, pistons, and valves (Dhar *et al.*, 2012).

1.4 Problems Encounter in the Biodiesel Production

For biodiesel production, high FFA and water content in the oil are the two limitations of transesterifying vegetable oils with alcohol using conventional alkaline catalyst (Ma & Hana, 1999; Satyarthi *et al.*, 2010; Thiruvengadaravi *et al.*, 2012). High acidic oils normally present high amounts of free fatty acids (FFA), varying from 3% to 40%, which make non-recommendable its usage with the conventional technology that employs a basic homogeneous catalyst (Chung *et al.*, 2008). There are advantages and limitations of the conventional methods in transesterification using low quality oil. This give rise the search for alternative approaches.

For biodiesel quality monitoring, the problem and limitation of current analysis technology is cost and the availability of advanced facilities which is not available on engine operation site. The analysis methods and analysis devices utilizing gas chromatography and FTIR have some disadvantages, such as sample preparation, which is time consuming, use of more than one internal standard, a longer analysis time, and an expensive technique employed (Soares *et al.*, 2008; Kay *et al.*, 2012). Therefore, development of alternative methods that combine low cost, fast and accurate results and portability is necessary as alternative approaches.

1.5 Hypothesis

To solve the biodiesel production problem as mentioned, it is necessary to develop a new heterogeneous catalysts, which has, high FFA and water-tolerance that could show promising performances in terms of methyl ester (biodiesel) yield, reaction conversion, potentiality and sustainability, as well as simplicity to greatly simplify the biodiesel refining process.

As a solution for biodiesel quality monitoring, there is necessary to develop a new biodiesel test kit and triglyceride test kit to providing fast, simple and affordable *in situ* fast check analysis in measuring FAME content in diesel & triglycerides content in final FAME product economically.

1.6 Objectives

The objectives of this study were as follows:

- a. to develop a new heterogeneous catalytic approach for the biodiesel production,
- b. to develop new fast check test kit for biodiesel blending percentage monitoring and triglycerides content of biodiesel purity monitoring
- c. to determine the quality of biodiesel, and
- d. to determine biodiesel percentage of biodiesel-diesel blend

1.7 Scope of Study

In this study, removal of FFA and water by natural zeolite and modified zeolite were carried out on the crude jatropha oil sample through adsorption (batch) experiments under different experimental conditions, namely varying shaking time, initial FFA or water concentration and solid – solution ratio. The effect of zeolite modification on transesterifications was investigated at different reaction time, type of cation saturation on zeolite, temperature, catalyst dosage, methanol – oil ratio and particle size of zeolite. Also, physical and chemical characteristics were investigated for all sample of oil, biodiesel and diesel fuel according to EN 14214 and ASTM D6751. Subsequently, performance (Brake specific fuel consumption, BSFC and brake thermal efficiency, BTE, exhaust gas temperature, EGT) and emission characteristics (smoke density) of these biodiesel with diesel fuel were examined and compared in a direct injection (DI) diesel engine. Apart from that, Biodiesel Test Kit and Triglycerides Test Kit were invented to develop *in situ* fast check analysis methods which provide fast, simple and affordable *in situ* fast check analysis in measuring FAME content in diesel & triglycerides content in final FAME product, respectively.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Biodiesel

Depletion of world petroleum reserves and the impact of environmental pollution of increasing exhaust emissions have led to the search for suitable alternative fuels for diesel engines such as biodiesel are being increasingly sought (Demirbas, 2011; Koh and Ghazi, 2011; Taufiq-Yap *et al.*, 2011; Salvi and Panwar, 2012; Ismail *et al.*, 2013). There are various reasons for the search of an alternative fuel that is technically feasible, environmentally acceptable, economically competitive, and readily available (Talebian-Kiakalaieh *et al.*, 2013). Biodiesel is receiving increasing attention as an alternative, renewable, non-toxic, biodegradable, carbon neutral and environmentally benign fuel for diesel engines has been attracting considerable interest all over the world which can significantly reduce global warming and the dependence on conventional fossil fuels (Singh and Singh, 2010; Ahmad *et al.*, 2011; Chakraborty *et al.*, 2011; Lam *et al.*, 2010; Atabani *et al.*, 2013; Yaakob *et al.*, 2013; Yahyaee *et al.*, 2013).

Biodiesel is a diesel fuel alternative produced from vegetable oils and animal fats (Fukuda *et al.*, 2001). Biodiesel defined by ASTM as the mono alkyl ester produced from vegetable oils or animal fats, one of the most promising alternatives (Marchetti and Errazu, 2010). Biodiesel is a mixture of mono alkyl esters of long-chain (C16-C18) fatty acids, usually methyl or ethyl esters, obtained by transesterification of the triglycerides contained in vegetable oils and animals fats (Salamanca *et al.*, 2012). Biodiesel can be used as fuel for diesel engines, either neat or when blended with petroleum diesel (Fernanda *et al.*, 2006; Nbia *et al.*, 2007). Biodiesel can be used pure or mixed with petroleum distillates to attain blends defined with the abbreviation BX, where X stands for the biodiesel percentage (v/v). The designation of pure biodiesel is B100 and the mixtures are named by the BXX abbreviation, which indicates the B100 volume (in percent) in the mixture with diesel (Ragonesea *et al.*, 2009).